Ab initio and Molecular Dynamic models of displacement damage in crystalline and turbostratic graphite

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This thesis is dedicated to my parents.

For their support and encouragement
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Alice J. McKenna
January 8, 2016
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Abstract

One of the functions of graphite is as a moderator in several nuclear reactor designs, including the Advanced Gas–cooled Reactor (AGR). In the reactor graphite is used to thermalise the neutrons produced in the fission reaction thus allowing a self–sustained reaction to occur. The graphite blocks, acting as the moderator, are constantly irradiated and consequently suffer damage. This thesis examines the types of damage caused using molecular dynamic (MD) simulations and \textit{ab initio} calculations.

Neutron damage starts with a primary knock–on atom (PKA), which is travelling so fast that it creates damage through electronic and thermal excitation (this is addressed with thermal spike simulations). When the PKA has lost energy the subsequent cascade is based on ballistic atomic displacement. These two types of simulations were performed on single crystal graphite and other carbon structures such as diamond and amorphous carbon as a comparison.

The thermal spike in single crystal graphite produced results which varied from no defects to a small number of permanent defects in the structure. It is only at the high energy range that more damage is seen but these energies are less likely to occur in the nuclear reactor. The thermal spike does not create damage but it is possible that it can heal damaged sections of the graphite, which can be demonstrated with the motion of the defects when a thermal spike is applied.

The cascade simulations create more damage than the thermal spike even though less energy is applied to the system. A new damage function is found with a threshold region that varies with the square root of energy in excess of the energy threshold. This is further broken down in to contributions from primary and subsequent knock-on atoms. The threshold displacement energy (TDE) is found to be $E_d = 25$ eV at 300 K. In both these types of simulation graphite acts very differently to the other carbon structures.

There are two types of polycrystalline graphite structures which simulations have been
performed on. The difference between the two is at the grain boundaries with one having
dangling bonds and the other one being bonded. The cascade showed the grain boundaries
acting as a trap for the knock-on atoms which produces more damage compared with the
single crystal.

Finally the effects of turbostratic disorder on damage is considered. Density functional
theory (DFT) was used to look at interstitials in (002) twist boundaries and how they
act compared to $AB$ stacked graphite. The results of these calculations show that the
spiro interstitial is more stable in these grain boundaries, so at temperatures where the
interstitial can migrate along the $c$ direction they will segregate to (002) twist boundaries.
Publications and Presentations

Publications


Presentations

Oral


- Postgraduate Research Conference 2014, University of Surrey *Understanding degradation in a nuclear reactor material*, February 2014.

- International Nuclear Graphite Specialists Meeting (INGSM14), Seattle (USA), *Density functional theory (DFT): Point defects in (002) twist boundaries in graphite*, September 2013.
• International Conference on Intergranular and Interphase Boundaries in Materials (iib13), Halkidiki (Greece), *Density functional theory (DFT): Point defects in (002) twist boundaries in graphite*, June 2013.

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**Poster**

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• NanoteC12, University of Sussex, *Radiation damage in nuclear graphite*, August 2012.

• CCP5 methods in molecular simulation, Cardiff University, *DFT calculation of point defects in (002) twist boundaries in graphite*, August 2012.
## Abbreviations

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<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>AGR</td>
<td>advanced gas-cooled reactor</td>
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<tr>
<td>AIMPro</td>
<td>\textit{ab initio} modelling program</td>
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<td>AIREBO</td>
<td>adaptive interaction REBO</td>
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<td>D</td>
<td>Dienes defect</td>
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<td>DFT</td>
<td>density functional theory</td>
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<td>EDIP</td>
<td>environment dependent interatomic potential</td>
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<td>ESP</td>
<td>electron stopping power</td>
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<td>FP</td>
<td>Frenkel pair</td>
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<td>GGA</td>
<td>generalised gradient approximation</td>
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<td>HF</td>
<td>Hartree-Fock</td>
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<td>HGH</td>
<td>Hartwigsen-Goedecker-Hutter</td>
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<td>HOPG</td>
<td>highly oriented pyrolytic graphite</td>
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<td>KP</td>
<td>Kinchin and Pease</td>
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<tr>
<td>LCBOP</td>
<td>long-range carbon bond order potential</td>
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<td>LDA</td>
<td>local density approximation</td>
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<td>LJ</td>
<td>Lennard-Jones</td>
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<td>MD</td>
<td>molecular dynamics</td>
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<td>PKA</td>
<td>primary knock–on atom</td>
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<td>PW</td>
<td>Perdew and Wang</td>
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<td>ReaxFF</td>
<td>reactive force field</td>
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<td>REBO</td>
<td>reactive empirical bond order</td>
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<td>Abbreviation</td>
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<tr>
<td>RRA</td>
<td>relative rotation angle</td>
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<td>Schrödinger equation</td>
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<td>SKA</td>
<td>secondary knock-on atom</td>
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<td>STDEV</td>
<td>standard deviation</td>
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<td>ta-C</td>
<td>tetrahedral amorphous carbon</td>
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<td>TDE</td>
<td>threshold displacement energy</td>
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<td>TKA</td>
<td>tertiary knock-on atom</td>
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<td>TS</td>
<td>transition state</td>
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<tr>
<td>VASP</td>
<td>Vienna <em>ab initio</em> simulation package</td>
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<tr>
<td>ZBL</td>
<td>Ziegler-Biersack-Littmarck</td>
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Chapter 1

Introduction

This project is to look at different types of damage for irradiated graphite in a nuclear reactor. Molecular dynamic (MD) simulations were performed to represent the damage produced, in the nuclear reactor, to the graphite. Also \textit{ab initio} calculations were used to look at the properties of the damage produced in the graphite.

1.1 Nuclear reactors

Nuclear power in the UK generates $\sim 18\%$ \cite{1} of the power used in the country. In the late 1990’s reactors powered close to $25\%$ of the annual electricity used. This number has gone down due to the old plants shutting down \cite{1}. The history of nuclear reactors goes all the way back to the Manhattan project. On December 2\textsuperscript{nd} 1942 the first self-sustaining nuclear reaction was achieved by an Italian physicist E. Fermi \cite{2}. This atomic pile is now known as the first nuclear reactor.

The main nuclear reactor type in the UK is the advanced gas–cooled reactor also known as the AGR (Figure 1.1(a)). The AGR is the second generation of nuclear reactors in the UK; the first was the Magnox reactor. Currently there are 16 nuclear reactors running (14 of these are AGR’s), the majority of these will be retired by 2023 \cite{1}.

For the current nuclear reactors water is pumped into the pipes which travel into the reactor. The water is then heated up, producing steam which then turns the generators that produce the power. In the reactor fuel stringers and control rods are placed in the graphite blocks. The graphite acts as a moderator; an example of its structure before the fuel is inserted can be seen in Figure 1.1(b). The purpose of the moderator is to thermalise
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Figure 1.1: Images about AGR’s where (a) is a schematic of an AGR (image from website [3]) and (b) is the graphite core from an AGR before the fuel insertion (image from website [4]).

the neutrons that are produced in the fission reaction. Not only does the graphite act as a moderator but it also is an important structural and thermal management component.

The new build in the UK for nuclear reactors will not be using graphite, but the USA announced its Next Generation Nuclear Program which includes graphite moderated advanced high temperature reactors. This is to be built at the Idaho National Laboratory in 2021 [5]. China’s Institute for Nuclear and New Energy Technology (INET) is currently building a high temperature graphite reactor (HTR) [6].

1.1.1 Neutron moderator

The thermalisation of the fission neutrons is done to increase the cross-section for $^{235}U$ fission thus making it more probable for further fission reactions to happen. This means that a self sustained reaction can occur in the reactor. An example of a fission reaction that can occur in a reactor is shown in equation (1.1)

$$^{235}U + n_{\text{slow}} \rightarrow ^{236}U \rightarrow ^{142}Ba + ^{92}Kr + 2n_{\text{fast}}$$ (1.1)

This reaction shows the smaller nuclei produced after the uranium atom splits are very neutron heavy isotopes because the most abundant isotopes for barium and krypton are $^{138}Ba$ and $^{84}Kr$ respectively.

The typical initial energy of the neutron emitted during fission of $^{235}U$ is $(1–2)$ MeV [7] which can be clearly seen in Figure 1.2 which is from ‘Nuclear Physics and Reactor Theory’ by the U.S. Department on Energy [7]. On average 15 % of the neutrons’ kinetic energy is
transferred to a carbon nucleus in each collision. If the neutron energy is 2 MeV, its first collision will lose 300 keV. This leaves a neutron with an energy of 1.7 MeV, so on the second collision it will transfer 255 keV to the carbon nucleus. It will take $\sim 100$ collisions for the neutron to thermalise (i.e. have the same kinetic energy as the graphite nuclei with which it collides).

1.2 Graphite

Graphite is part of a family of sp$^2$ hybridised carbon materials, which includes fullerenes (the buckyball, C60, etc [8]), carbon nanotubes [9] and others such as nanocones [10]. Diamond is an sp$^3$ hybridised allotrope of carbon and there are various kinds of amorphous carbon which combine sp$^3$ and sp$^2$ carbon in various proportions [11].

Graphite is the most stable form of carbon under ambient conditions and is made up of layers of sp$^2$ carbon atoms known as graphene. Graphene is the most recently discovered allotrope of carbon, discovered at Manchester by Novoselov et al. [12]. The structure of graphite was first looked at by Hull via x-ray [13], but it was not until 1924 that it was proposed by Bernal to be made up of layers of hexagon honeycomb [14]. These layers of graphene are strong due to the covalent bonding between the carbon atoms. In graphite the nearest neighbour distance is 1.42 Å [15]. The force between the layers is currently thought to be the Van der Waals force [16] with the interlayer space of 3.35 Å [17] and a
binding energy 35 meV [18].

The layers of graphite are usually stacked in an \( AB \) sequence along the \( c \) axis but they can be in an \( ABC \) (rhombohedral) sequence or even an \( AA \) stacking sequence [19]. Due to this stacking sequence of \( AB \) there are two types of lattice sites, the \( \alpha \) and \( \beta \) sites shown in Figure 1.3. If the \( c \)-axis is vertical then an \( \alpha \) will have an atom above and below (red) whereas the \( \beta \) site sits above and below hexagon centres (blue).

A macroscopic single crystal graphite is unobtainable but there are alternatives such as natural graphite, kish graphite or synthetic graphite. The latter includes highly oriented Pyrolytic graphite (HOPG). The definition of Pyrolytic graphite is given in ‘Recommended terminology for the description of carbon as a solid’ [20], as graphite with a “high degree of preferred crystallographic orientation of the \( c \)-axes perpendicular to the surface of the substrate”. When this Pyrolytic graphite is put under stress at high temperatures the result is this HOPG. The result is a mosaic of crystallites with random orientations in the basal plane, but highly aligned in the \( c \) direction. Since many properties of graphite are isotropic in the basal direction, this material is generally regarded as a reasonable substitute for the single crystal.

The single crystal is highly anisotropic and very weak in shear. Graphite grades for nuclear reactors are polygranular and made to be as isotropic as possible for strength and uniformity. They have high chemical purity to reduce neutron absorption and to reduce the amount of activation acquired in service.
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1.3 Process

In the nuclear reactor the graphite moderator is irradiated. In Figure 1.4 it shows the physical process of what is happening in the graphite when a fast neutron (released from the fission reaction) collides with a carbon atom. When the carbon atom is hit by the neutron it is displaced from its original site. The carbon atom that is initially displaced is known as the primary knock-on atom (PKA) [21].

This PKA will travel through the graphite without colliding with any of the surrounding carbon atoms. The reason for this is due to its high energy; the only way for the PKA to lose energy is to transfer some of its kinetic energy via the electrons. This is the swift heavy ion regime, as described by Schwen and Bringa for irradiation in graphite and diamond [22] and by Marks et al. in titania [23]. This region is simulated here with a thermal spike as shown in Figure 1.5(a). There have been no publications in relation to thermal spike simulations through graphite, but there have been simulations of other carbon materials. One paper is on the simulation of tetrahedral amorphous carbon (ta-C) produced by Marks [24], which showed liquid quenching cooling rate is fast $t_{cooling} \sim 1 \text{ ps}$ and the quenching time is proportional to the radius of the spike. Then Sorkin et al. simulated thermal spikes through diamond at a high temperature, finding the simulated damaged region is highly inhomogeneous [25]. As the temperature increases the fraction of three-coordinated atoms and two-coordinated atoms also increases.

When the PKA has lost enough energy it will collide with carbon nuclei, which will hit other carbon nuclei which then starts a cascade (Figure 1.5(b)). These cascades are also
known as secondary displacement groups. At the start of this project there were virtually no publications on cascades in bulk graphite, however, there are some that focus on the surface of the graphite. One example is Smith’s paper looking at the bombardment of graphite and diamond, which showed that atoms require less energy in diamond compared to graphite in order to be ejected [26]. Recently Christie et al. ran radiation damage cascade simulations in graphite [27], showing how cascades in graphite act very differently to other carbon materials.

With each collision the energy of the PKA will decrease until it reaches the threshold displacement energy (TDE). This is the minimum energy required to create a Frenkel pair (FP) [28]. Simulations to evaluate TDE are basically the same as the cascade simulations but with a lower energy 1.5(c). There have been a few simulations working on finding the value for the TDE of graphite: these are discussed later in Chapter 4.3 and highlighted in Table 4.4.

As mentioned earlier it will take \( \sim 100 \) collisions to thermalise the neutron. This means a hundred PKA’s are created per neutron, leading to lots of damage in the bulk graphite of the moderator.

### 1.4 Nature of damage

This irradiation will cause different types of damage to the graphite bricks in the reactor, which can affect the structure. There have been many publications on the changing shape
of graphite when irradiated at different temperatures. The dimensional change of HOPG can be seen clearly in the plot produced by Kelly et al. [29] shown in Figure 1.6. The plot shows that there is expansion in the \( c \) direction and contraction in the \( a \) direction. The change in dimensions of HOPG at lower temperatures (below 250 C) exhibit a sigmoidal trend but at the higher temperatures there is a linear trend with the neutron dose. Hinman et al. has shown the expansion in the \( c \) axis is mainly due to the interstitial clusters at high temperatures [30].

Many investigations have gone into the different types of damage created in the irradiated graphite, both theoretical [31] and experimental [32, 33]. The standard model explains this \( c \)-axis expansion by the migration of point defects, which is explained in more detail later in this chapter.
1.4.1 Point defects

The primary defect formed under irradiation is a Frenkel pair. This comprises of a single self interstitial and a single vacancy. An interstitial is where there is an extra atom in the lattice and a vacancy is where there is an atom missing from its lattice site. There has been a considerable body of work on the energies of these point defects shown in the review by Thrower and Mayer [34].

There are four forms of single self interstitial atoms: these are shown in Figure 1.7. These are called spiro, grafted (also known as bridge), $\alpha$–split and the $\beta$–split [35] (also known as dumbbell). The spiro structure (Figure 1.7(a)) gets its name due to its resemblance to the spiropentane molecule. It is bonded to both layers. The grafted structure (Figure 1.7(b)) is grafted to one layer of graphene. The split structure (Figure 1.7(c)) arises where the interstitial and a host atom share the same (host atom) site is named depending on whether it is either an $\alpha$ or $\beta$ site.

There are not just single self interstitials, there are also di-interstitials which have been studied by Latham et al. [36]. Some of the di-interstitial structures seen in graphite are the twin–triangle, bent bridge, bi–pentagon, skew bi–pentagon, grafted intralayer and the split pair. Figure 1.8 shows some examples of these di-interstitials.

Another single defect is the vacancy [37] which can be either in an $\alpha$ or a $\beta$ site. The structure of a vacancy in a graphene layer can be seen in Figure 1.9(a), which shows an atom missing from the $\alpha$ site. The $\beta$ vacancy looks the same, the only difference is whether there are atoms above and below the vacancy site. Another defect that can be seen in a layer of graphene is the Dienes (D) defect [38] also known as the Stone–Wales defect [39] or the Stone–Thrower–Wales defect. This defect has no extra or less atoms but it is where
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(a)  
(b)  
(c)  

Figure 1.8: Types of di-interstitials highlighted in red, (a) bent interlayer bridge defect (b) bi-pentagon interlayer bridge defect and (c) rearranged grafted intralayer bridge (isolated pentagon defect).

(a)  
(b)  

Figure 1.9: Point defects in a layer of graphene, (a) single α vacancy structure and (b) Dienes defect, with the red highlighting the rotated bond.

a bond has been rotated 90°. An example of this defect can be seen in Figure 1.9(b) with the rotated bond highlighted in red.

The intimate FP is where a self interstitial and a vacancy can coexist without annihilating [40]. There are two forms of FP, with the difference between the two depending on the vacancy site. The vacancy can be either in an α site or a β site. The FP structure can be seen in Figure 1.10, where in this example the vacancy in the β site. These point defects can create stacking faults as seen in Telling et al.’s paper where the defect shear the layers so that they are no longer in the AB stacking sequence [41].

In graphite that has been irradiated a single defect is rarely seen by itself, instead they tend to congregate creating loops and clusters. Thrower has published images of these interstitial loops which can be seen in Figure 1.11. This image shows large loops that come from the aggregation of interstitials [32]. There is also speckling seen in the photo which is caused by the small vacancy loops in the basal plane.
1.4.2 Extended defects

As mentioned the aggregation of point defects can create certain extended defects. The interstitial loops have been observed in other research, such as Ohr’s experiment on electron damage in graphite [42]. It is only that interstitials and vacancies can coalesce into pris-
matic loops of interstitial and vacancy kind respectively, but also vacancies can aggregate to create an extended interplanar link between the layers (also known as ramp defect). An example of this is shown in Figure 1.12 which is from Trevethan et al.’s calculations on the aggregation of vacancies [43, 44]. In addition Trevethan et al. showed that vacancies can aggregate into lines, which cause the basal layer contraction evident in the lower half of Figure 1.6 [45].

A recent additional mechanism for dimensional change is the buckle, ruck and tuck mechanism by Heggie et al. [46]. This means that the role of line defects has a more prominent effect on dimensional change. The main one is the basal edge dislocation which glides between graphite layers and has been shown to be generated and moved during neutron irradiation [34]. When two dislocations of opposite sign glide they will interact and cause buckling. This buckling will increase the $c$-axis dimension and decreases one of the basal dimensions. The buckle in the graphite is held by interlayer bonds [41] or it can be held by interstitials or interlayer divacancies. The interlayer bonds are not stable at 250 C, which means that the large and sigmoidal expansion in the $c$ dimension (Figure 1.6), disappears. When the temperature is above 250 C then it is possible for the edge dislocations to glide together and create a ruck. This ruck will absorb further basal dislocations and will extend. This has been called the ruck and tuck defect and is a line defect. In addition to the standard mechanism for $c$-axis dimensional change, this process adds to it linearly with neutron dose.

The final extended defect to be discussed, beyond line defects and aggregates of point defects, is the grain boundary, which is the two dimensional interface between two graphite crystallites that are misoriented and/or displaced with respect to one another. The two types of grain boundaries are tilt and twist depending on whether the misorientation angle is defined about an axis within the boundary (tilt) or perpendicular to it (twist). The tilt boundary will either be symmetric or asymmetric. An example of the symmetric tilt
boundaries from Liu et al.’s molecular dynamic simulations [47, 48] is shown in Figure 1.13. Symmetric tilt has a mirror reflection in the boundary plane; they are also called twin interfaces. These were first reported in detail in 1941 by Palache [49], there are three basic types of twin interface in graphite [50]. Then with the asymmetric tilt boundaries these are not mirror reflections of the plane of perfect crystal. The twist boundary is also divided up into symmetric and asymmetric. A symmetric pure twist boundary is a symmetric twist of 180°. The asymmetric twist is the most general boundary, as it is an asymmetric tilt that has a further twist about the boundary normal.

The (002) twist boundary has been discussed since the early diffraction work on graphite, due to Franklin [51], Bacon [52, 53] and others. They realised that in order to fit (002) diffraction intensity profiles they needed to account for a variation between 3.354 Å for a very perfect specimen to 3.44 Å for a less well ordered specimen. The disordering is associated with rotation in the stacking arrangements and they associated a variable $p$ to it, which goes from 0 (perfect) to 1 (most rotational disorder, or turbostratic). Each layer which is not $AB$ stacked gives rise to a higher interlayer spacing. The position of the maximum intensity of the (002) spot gives the value of $p$. 

Figure 1.13: Symmetric tilt boundary structures in graphite taken from Liu's paper [47]. These range from a tilt angle of 23° to 30° from left to right.
The fundamental defect in rotational disorder is the (002) twist boundary, which is where one layer has a relative rotation compared with its neighbour. Small angles of rotation give rise to a Moiré interference pattern, shown in Figure 1.14 produced by Campanera et al. [54]. It is clear from visual inspection of the pattern that there are interlayer

![Moiré patterns with different rotation angles](image)

Figure 1.14: Images of Moiré patterns with different relative rotation angles about a β site produced by Campanera et al. [54].
locations where bonds in one layer cross bonds in the neighbouring layer at approximately 90\degree. A spirointerstitial is close in nature to spiropentane, but in \( AB \) graphite the two triangles of C-C bonds lie at 60\degree to one another, whereas in spiropentane, where they are not constrained, they are at 90\degree. Therefore it was reasoned that at such sites in a twist boundary, the spiro-interstitial should have a lower energy and this is what we set out to test with DFT calculation (see Chapter 6).

1.5 Simulations and Calculations

This is a theoretical project that uses molecular dynamic (MD) simulation and \textit{ab initio} calculations, to look at radiation damage in graphite. There are different types of damage in graphite seen in the literature and the MD simulations will show how they are formed. Then a more detailed investigation of the types damage will be done via \textit{ab initio} calculations.

In Chapter 2 the theory behind molecular dynamic (MD) simulation will be explained. With a section on the environmental dependent interatomic potential (EDIP) which is the potential used in this study as well as the Ziegler–Biersack–Littmarck (ZBL) potential. The EDIP and ZBL potential were used to simulate radiation damage in single crystal and polycrystalline graphite.

Then in Chapter 3 the theory behind \textit{ab initio} density functional theory (DFT) calculations will be explained, with a section on \textit{ab initio} modelling program (AIMPRO) with filtration as this was used for the quantum mechanical analysis of the damaged structures.
Chapter 2

MD theoretical background

Molecular dynamic (MD) simulation is a technique for looking at the equilibrium and transport properties of a system using classical mechanics. MD simulation is a way of complementing experiment and theory. The first paper on MD cascade simulation by Gibson et al. was the simulation of radiation damage in copper [55]. The general idea behind MD is a system of N particles is used and Newton’s equation of motion is solved until all the properties in the system do not change with time, this is known as equilibration. Once the system is equilibrated then the measurements can be made.

2.1 Introduction

The key stages of a MD simulation can be seen in the flow diagram (Figure 2.1). This starts with the set up of the initial system: which consists of the position and initial velocity of each atom. Then the atomic force is calculated based on the potential method. The atomic motion for each time step is then calculated by integration using an algorithm. The physical properties are calculated; this is all then repeated until the required time for the simulation has been attained.

2.1.1 Integration of the Newtonian equation of motion

To calculate the force between the particles Newton’s equation of motion is integrated over time. In 1977 new algorithms were introduced for the integration in MD [56]. There are now a number of algorithms designed to perform this integration. These algorithms
are derived by starting from the Taylor expansion of the coordinates of a particle at $t$:

$$x(t + \Delta t) = x(t) + v(t)\Delta t + \frac{f(t)}{2m} \Delta t^2 + \frac{\Delta t^3}{3!} \cdot \dddot{x} + O(\Delta t^4)$$  \hspace{1cm} (2.1)$$

For the MD simulations in this project the velocity Verlet algorithm is used. This is based on the Verlet algorithm (1967) \cite{57}, shown in equations 2.2 and 2.3.

$$x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \frac{f(t)}{m} \Delta t^2$$  \hspace{1cm} (2.2)$$

$$v(t) = \frac{x(t + \Delta t) - x(t - \Delta t)}{2\Delta t}$$  \hspace{1cm} (2.3)$$

Where $x$ is the position, $t$ is the time, $\Delta t$ is the time step, $f$ is the force and $m$ is the mass. The velocity using this method is only accurate to an order of $\Delta t^2$. For a more accurate velocity a Verlet like algorithm must be used, like the velocity-Verlet algorithm. The velocity form of the Verlet algorithm was done by Swope \textit{et al.} \cite{58} seen in equation 2.4 and 2.5.

$$x(t + \Delta t) = x(t) + v(t)\Delta t + \frac{f(t)}{2m} \Delta t$$  \hspace{1cm} (2.4)$$
The velocity Verlet method is not self-starting so a single Euler step is needed because the single Euler step will produce a force that can then be used to start the velocity Verlet algorithm. The Euler algorithm involves the Taylor expansion truncated at $\Delta t^2$ shown in equation 2.6 and 2.7.

$$x(t + \Delta t) = x(t) + v(t) \delta t + \frac{f(t)}{2m} \Delta t$$

(2.6)

$$v(t + \Delta t) = v(t) + \frac{f(t + \Delta t) + f(t)}{2m} \Delta t$$

(2.7)

2.1.2 Thermodynamic ensembles

In a standard MD simulation all frames are microstates of the microcanonical (NVE ensemble). The NVE stands for a constant number of particles (N), constant volume of the cell (V) and constant total energy (E). The code would normally store the total energy as the potential and kinetic energy. Temperature is hard to defined in this case. For the initial equilibration stage, the velocity is scaled to adjust the temperature through the kinetic energy. This takes/gives energy to the system so that the temperature is maintained, which means these frames are not used as part of the ensemble averages. MD simulations are run in two stages. The first is the equilibration where the correct temperature for the simulation is produced. The second part is the production NVE run for the ensemble sampling.

2.1.3 Energy and force

There are several ways to calculate the energy of a system:

- Force fields typically use harmonic expressions to describe the bond breaking and stretching.
- Pair potentials, which include the Lennard–Jones (LJ) potential, the total energy is the sum over all pairs of atoms, shown by the plot in Figure 2.2. When the potential is long-ranged it is sometimes truncated and shifted in energy for computational speed.
- Many-body potentials such as EDIP are analytical potentials with higher order terms.
- Tight-binding is the simplest method that includes electrons in the simulations. It is a quantum mechanical calculation where important integrals are parameterised or...
CHAPTER 2. MD THEORETICAL BACKGROUND

Figure 2.2: The Lennard–Jones (LJ) potential plot of the total energy over the separation of atoms. The intermolecular potential is \( V(r) = 4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \) where \( \epsilon \) is the well depth and measures how much the two particles attract each other. The distance at which the molecular potential between the two particles is zero is \( \sigma \) and \( r \) is the distance between the two particles.

...calculated in a simplified way. Equivalent chemical methods are Extended Huckel Theory and the *NDO methods (CNDO, INDO,...).

• *Ab initio* is a method that uses no experimental parameters, the energy is calculated from first principles based on the laws of quantum mechanics. An example of this is the density functional method.

There is a trade off between accuracy and computational cost.

2.1.4 Periodic boundary conditions

Periodic boundary conditions are an essential part of an MD simulations. As a bulk material is generally produced by repeating a primitive cell. This repeat is shown in Figure 2.3 with the initial cell highlighted in red. Due to the periodic boundary there is a wrap around. This is shown by the interaction of atoms \( i \) and \( j \) as they are next to each other in the block next to the block they occupy. This means that during the simulations the displaced atoms should not interact with the boundaries.

2.2 Interaction potentials for carbon

There have been very few publications on molecular dynamic (MD) simulations in carbon, especially simulations of radiation damage in graphite. It is surprising there is so little
work with MD for irradiated graphite, given that graphite was the first nuclear moderator. MD and Monte Carlo have a heritage that extends back to the Manhattan project in 1942. The very first MD simulation was on radiation damage in metals seen in the paper written by Gibson et al. [55]. There is now a vast literature on damage in metals and oxides. Even though graphite has been very important in the nuclear industry, particularly in the UK and now in the US, it has only been in the last ten years that suitable MD potentials for carbon have started to be developed. The difficulty of carbon with its near degenerate allotropes having vastly different hybridisation and geometry has always been a challenge for interatomic potentials, and it is only in the last decade that truly credible potentials have been developed. These interatomic potentials for carbon stem from the original work of Abell [59] and Tersoff [60].

- Tersoff potential [60]
  First he released a potential for silicon in 1986 then in 1988 for carbon. This was the first method that treated multiple hybridisation states. This is a short range potential which employs a switch function to identify the nearest neighbours. This method is computationally efficient but inverts the density relationship between graphite and diamond because the interlayer distance is unphysically low.

- Brenner Reactive Bond Order (REBO) potential [61]
  Drawing from Tersoff, Brenner soon released his REBO potential which added hydrogen interactions and improved the descriptions of radicals. This was originally
developed for chemical vapour deposition of diamond simulation. The potential cannot simulate the pathway for bond formation and breaking.

- One step beyond Tersoff-Brenner potential [62]
  There have been a few adaptions to this potential such as Nordlund who in 1996 included a long–range extension to the potential, for the graphitic layers [63]. There was also Smith and Beardmore who splined a Lennard-Jones (LJ) potential to the Tersoff and Brenner potential for atoms that are not covalently bonded [64].

- Adaptive Interaction REBO (AIREBO) potential [65]
  The Lennard-Jones (LJ) interaction used to describe the long-range interaction between the sp² sheets is grafted on to REBO with a switching function. This potential allows for breaking and making of covalent bonds while making changes to the atomic hybridisation within a classical potential.

- Environment Dependent Interaction Potential (EDIP) [66]
  This potential was adapted from an earlier silicon version employing atom–centred bond–order. This involved three steps: a non bonding term (increase graphite c–spacing), dihedral rotation penalties for π–bonding atoms, and a variable–range pair interaction. This is a fast and robust potential but does not have long–range attraction and it does not penalise isolated sp² atoms which should have raised energy by being π radicals. The formalism for this potential, which is the workhorse for MD in this thesis, is presented in the next section.

- Reactive Force Field (ReaxFF) [67]
  The framework is as general as possible so captures all conceivable interactions from covalent to Coulomb. ReaxFF can also be used to describe other chemical species but is not as accurate as others when carbon is in a liquid state.

- Long–range Carbon Bond Order Potential (LCBOP) [68]
  This is the best system for a pure carbon system as it is similar to AIREBO but has parameter fitting and functional form like EDIP. The interlayer attraction and related properties compare well with experimental results.

As well as empirical potentials there are also electronic structure techniques such as density functional theory (DFT).
CHAPTER 2. MD THEORETICAL BACKGROUND

2.3 Environment Dependent Interaction Potential (EDIP)

The empirical potential used in this project was the environment dependent interaction potential (EDIP). This empirical potential was developed by Marks [66]. It was originally developed for silicon (Si) [69] and was adapted for carbon (C). The silicon EDIP was derived by the inversion of ab initio cohesive energy curves, its main weakness is the π–bonding effects. EDIP is used mainly to describe the chemical bonding regime, which applies to internuclear distances between 1–3 Å.

2.3.1 The model

The functional form consists of three components: a two–body pair energy ($U_2$), three–body angular penalty ($U_3$) and a generalised measure of coordination ($Z$). These can be seen in the total energy in equation (2.8).

\[
U_i = \sum_i U_2(r_{ij}, Z_j) + \sum_{j<k} U_3(r_{ij}, r_{ik}, \theta_{ijk}, Z_i) \tag{2.8}
\]

The $Z_i$ consists of a spherical contribution $z_i$ and an aspherical term. There is no aspherical term for graphite or diamond due to the symmetrical structure.

The two–body pair potential is for short range that will decay to zero if the distance is smaller than the cutoff (parameter $a'$). In equation (2.9) the exponential term $-\beta Z^2$ describes the bond order.

\[
U_2(r, Z) = \epsilon \left[ \left( \frac{B}{r} \right)^4 - e^{-\beta Z^2} \right] \exp \left( \frac{\sigma}{r - a - a' Z} \right) \tag{2.9}
\]

Then in the three–body potential there are radial and angular terms for distances of $r_{ij}$ and $r_{ik}$. All the terms for this part of the potential are in equation (2.10). The term $\tau(Z)$ describes the variation in the ideal bonding angle, $\tau(Z) = 1 - \frac{Z}{12} \tanh[t_1(Z_1 - t_2)]$.

\[
U_3(r_{ij}, r_{ik}, \theta, Z) = \lambda(Z)g(r_{ij}, Z)g(r_{ik}, Z)h(\theta, Z) \\
\lambda(Z) = \lambda_0 \exp[-\lambda'(Z - Z_0)^2] \\
g(r, Z) = \exp \left[ \frac{\gamma}{r - a - a' Z} \right] \\
h(\theta, Z) = 1 - \exp\{-q[\cos \theta + \tau(Z)]^2\} \tag{2.10}
\]

Where $\lambda(Z)$ is the magnitude function, $g(r_{ij}, Z)$ and $g(r_{ik}, Z)$ are the radial functions and $h(\theta, Z)$ is the angular term.
The spherical contribution \( z_i = \sum f(r_{ij}) \) where \( f(r) \) is a three parameter function, which for \( r < f_{\text{low}} \) is unity and \( r < f_{\text{high}} \) is 0 and between these it is equation (2.11)

\[
f(r) = \exp \left( \frac{\alpha}{1 - x^{-3}} \right)
\]

where \( x = (r - f_{\text{low}})/(f_{\text{high}} - f_{\text{low}}) \).

The generalized coordination \( Z_i \) defined below in equation (2.12)

\[
Z_i = z_i + \pi_3(z_i)X_{\text{dih}}^i + \pi_3(z_i)X_{\text{rep}}^i + \pi_2(z_i)X_{\text{rep}}^2
\]

where \( \pi_3 \) and \( \pi_2 \) are switching functions and \( X_{\text{dih}}^i \), \( X_{\text{rep}}^3 \), \( X_{\text{rep}}^2 \) describes dihedral rotation, \( \pi \)–repulsion at a three fold site and two fold site, respectively. Given by the equations (2.13) below.

\[
X_{\text{dih}}^i = Z_{\text{dih}}\Sigma \pi_3(Z_j)(\hat{R}_{jm} \cdot \hat{R}_{ik} \times \hat{R}_{il})^2C_{ijklm}^\text{dih}
\]

\[
X_{\text{rep}}^3 = Z_{\text{rep}}\Sigma \pi(Z_j)(\hat{R}_{ij} \cdot \hat{R}_{ik} \times \hat{R}_{il})^2C_{ijkl}^\text{rep3}
\]

\[
X_{\text{rep}}^2 = Z_{\text{rep}}\Sigma \pi(Z_j)[1 - (\hat{R}_{ij} \cdot \hat{R}_{ik})^2]C_{ijk}^\text{rep2}
\]

The distance–based cutoff functions \( C \) are shown in equations (2.14)

\[
C_{ijklm}^\text{dih} = p(R_{ij})p(R_{il})p(R_{jm})
\]

\[
C_{ijkl}^\text{rep3} = (R_{ij} - c_0)^2[1 - p(R_{ij})]p(R_{ik})p(R_{il})
\]

\[
C_{ijk}^\text{rep2} = (R_{ij} - c_0)^2[1 - p(R_{ij})]p(R_{ik})
\]

where the function \( p(r) \) is equivalent to the function \( f(r) \) but with different end points of \( p_{\text{low}}(r) \) and \( p_{\text{high}}(r) \).

The parameters mentioned here were published by Marks [70] and are shown in Table 2.1. EDIP uses an NVE ensemble, this means that in the simulation the number of carbon atoms stays constant as well as the volume of the cell simulated. The total energy should be conserved in MD simulations [71].

This potential was used due to its accurate description of bond making and breaking, which is needed for the irradiation simulations. It also produces good elastic properties and can describe the liquid state well [66]. There are some limitations of this empirical potential such as small rings (C\(^3\) triangles) being overly penalised, so will not be able to see the defect known as the spiro–interstitial (see Section 4.4). Another limitation is that there is no long–range attraction between the graphene sheets in the graphite cell (cutoff= 3.2 Å) against graphite interlayer separation of 3.35 Å.
CHAPTER 2. MD THEORETICAL BACKGROUND

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<td>$C_0$ (Å)</td>
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</tr>
</tbody>
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Table 2.1: The values for the parameters in EDIP from Marks paper [70]

2.4 Ziegler-Biersack-Littmarck (ZBL) potential

The Ziegler-Biersack-Littmarck (ZBL) potential is universally employed in ion implantation simulations [72]. As EDIP describes the chemical bonding regime, ZBL describes the nuclei–nuclei regime. So when the carbon atoms in the simulations get closer than 0.5 Å, EDIP switches to ZBL by using a smoothing spline.

2.4.1 The model

$V_{ZBL}$ is a Coulomb potential with a screening function ($\phi$) written as equation (2.15).

$$V_{zbl} = Z_1 Z_2 \frac{\epsilon^2}{4 \pi \epsilon_0} \frac{1}{r} \phi \left( \frac{r}{a} \right)$$  \hspace{1cm} (2.15)

where $Z_1$ and $Z_2$ are atomic numbers of the colliding nuclei separated by distance $r$ and $a$ is the length scale expressed in terms of the Bohr radius $a_0 = 0.529$ Å, shown in equation (2.16).

$$a = \frac{0.8853 a_0}{(\sqrt{Z_1} + \sqrt{Z_2})^3}$$  \hspace{1cm} (2.16)

There have been a few publications on simulations using ZBL with other potentials for carbon structures. The REBO hydrocarbon potentials was improved with ZBL by Kent et al. REBO [73], looking at sputtering. Also the Tersoff potential was improved by Nordlund et al. for looking at electron irradiated graphite [63]. Another example is with the
an adapted Tersoff and Brenner potential that is splined with a LJ potential by Smith and Beardmore [64].

### 2.5 EDIP and ZBL simulations

The MD simulation use both EDIP and ZBL potentials; the code switches between the two depending on the distance between the atoms using a Fermi scaling function \( f(E) \) (2.17).

\[
f(E) = \frac{1}{e^{E - E_f/KT} + 1}
\]

where \( E_f \) is the Fermi energy, \( K \) is the Boltzmann constant and \( T \) is temperature. The reason for switching between the two can be seen in the bottom plot in Figure 2.4. A Fermi scaling function is used to switch between EDIP and ZBL potential. The value for EDIP is \( r_{EDIP} = 1.05 \) Å, and ZBL is \( r_{ZBL} = 0.45 \) Å. This is shown in the plot in Figure 2.4 with \( w = 0.07 \) Å. This approach has been used in other EDIP simulations by Marks et al. [74] and Pearce et al. [75].

All the simulations use periodic boundary conditions within an NVE ensemble. The simulations are run in two stages. The first is the equilibration where the correct temper-
nature for the simulation is produced. The second part is the production run of NVE for the ensemble sampling.

The graphite structure for the simulations are made from an orthorhombic unit cell shown in Figure 2.5. This is made up of eight atoms (due to the \(AB\) stacking), which means there are four atoms in each layer. The blue box highlights the unit cell for one layer. The geometry used corresponds to the energy minimum for the EDIP potential, where the distance between the atoms is \(r = 1.421\ \text{Å}\), and the distance between the layers is \(c = 3.20\ \text{Å}\). The dimensions of the 8 atom orthorhombic cell are \(x = 3r\), \(y = \sqrt{3}r\) and \(z = 2c\).

For the simulations there are two types of cell setup both shown in Figure 2.6. Both these cells have fixed atoms in each layer to stop the layers from sliding as EDIP does not have any interlayer interaction (Van der Waals). These are represented with the green strip which is 1.5 Å wide meaning one atom is fixed in each layer. Then in the blue there is a thermostat (Berendsen thermostat [76] with a time-constant set at 100 times the timestep) which takes the excess energy from the simulation and is 3.0 Å wide (2 atoms wide). The thermostat is on each side of the fixed atoms due to the wrap around of the periodic boundary conditions. The thermostat rescales the velocity of the atoms, so that the temperature is constrained to within 13 % of the target temperature [66].

The first type of simulation is a thermal spike and is set up as shown in Figure 2.6(a). The thermal spike in this diagram is shown as a red cylinder whose radius can be changed. Each atom inside this cylinder is given the same energy in a pseudo-random direction. The simulations can be run to simulate different electronic stopping power \(\frac{dE}{dx}\). This is done by changing the radius of the spike and/or the energy given to each atom in the cylinder.
Figure 2.6: The set up for the two types of simulation (a) thermal spike and (b) cascade. In both set ups in each layer a strip of atoms (green) is held in place so that the layers do not slip and on each side of the fixed atom strip is a thermostat (blue). Highlighted in red there is (a) a cylinder which all of the atoms inside are given a velocity in different directions and (b) a sphere which is the locus of PKA starting positions, all with an initial velocity towards the centre of the sphere.

The simulations are run at a temperature which is set when the structure is equilibrated. This temperature goes up as a step function when the spike is first started.

The second type of simulation is a cascade and is set up as shown in Figure 2.6(b). After the cell has been equilibrated the PKA is pick from near the surface of the red sphere and is given a velocity towards the centre of the sphere. The cell size is chosen so that the cascade range is contained within the cell.

For each run the cell is quenched down to 0 K after the simulation has stabilised to check that the defect structures do not change.

In summary, this chapter has discussed MD simulation and detailed the EDIP method used for this project. In the following chapter, the first principles density functional code, AIMPRO is described.
Chapter 3

*Ab initio* theoretical background

Unlike MD which uses classical mechanics, electron structure methods use quantum mechanics. The energy and properties can be found using the Schrödinger equation (SE). These types of calculations are classed by how they are approximated; there are two main classifications. Semi-empirical methods use parameters obtained by experiments, which simplifies the calculations. Modern semi-empirical methods are based on the neglect of diatomic differential overlap (NDDO) method. Examples of these models are the modified neglect of diatomic overlap (MNDO) [77], the Austin model 1 (AM1) [78], and the parametric method number 3 (PM3). Then there is the *ab initio* method, which is what was used to run structural optimisations in this study. AIMPro was used for these calculations in this study.

### 3.1 Introduction

*Ab initio* calculation is a first principle calculation, which use no experimental parameters. The simplest *ab initio* calculation is a Hartree-Fock (HF) calculation. Hartree first performed these calculations in 1928, where he addressed the fact that for any atom or molecule there is more than one electron. The electron-electron repulsion terms mean that it is not possible to get an exact analytic solution for the Schrödinger equation (SE).

The time independent Schrödinger equation (SE) for one electron is written as equation (3.1)

\[ \hat{H} \Psi = E \Psi \]  

where \( \hat{H} \) is the Hamiltonian operator. \( \Psi \) is the total wave function of the system and \( E \)...
is the energy. The Hamiltonian is comprised of the kinetic energy \((T)\) of the nucleus \(N\) and electrons \((e)\) as well as the potential energy \((V)\) of the nucleus and the electrons. The SE is expressed as equation (3.2) for one atom of hydrogen which has only one electron.

\[
\frac{\hbar^2}{2m_e} \nabla^2 \Psi + (V - T) \Psi = 0 \tag{3.2}
\]

where \(\hbar\) is \(h/2\pi\) (\(h\) is Planck’s constant). The mass of an electron is expressed as \(m_e\). In a very accurate calculation \(m_e\) would be replaced by the reduced mass of the electron and the nucleus. The \(\nabla^2\) is the Laplace operator. This equation can be solved analytically for the hydrogen atom due to there only being one electron. When there is more than one electron in a system the calculation will become much more complex and must by and large be solved numerically.

For a many electron system the Hamiltonian will need to incorporate the three potential energies. The first is between the nuclei, the second is between the electrons and the third is between the nuclei and the electron. Also the kinetic energy of the nuclei and the electrons will need to be accounted for. The Hamiltonian with these components is expressed as follows in equation (3.3).

\[
\hat{H} = T_N + T_e + V_{NN} + V_{Ne} + V_{ee} \tag{3.3}
\]

### 3.1.1 Born-Oppenheimer approximation

The Hamiltonian (equation (3.3)) will need to be simplified for many electron atoms and molecules. The Born-Oppenheimer approximation is used because of the mass difference between the electron and the nuclei. This means that in a system the electron will be able to move much faster than the nuclei. So the approximation here is that the electrons move in the fields of fixed nuclei. This means that the kinetic energy of the nuclei will be zero and the potential energy for the nuclei nuclei interaction will be constant. With the Born-Oppenheimer approximation the Hamiltonian will be simplified to equation (3.4).

\[
\hat{H}_e = T_e + V_{Ne} + V_{ee} \tag{3.4}
\]

This new expression for the Hamiltonian is still very complex due to the inter electron potential \((V_{ee})\) and will require simplifying further, through other approximations.

The next sections will describe how this is further simplified. The first is the HF approximation and the other approach is with density functional theory (DFT).
CHAPTER 3. AB INITIO THEORETICAL BACKGROUND

3.2 Hartree-Fock

As mentioned above if you have a large system then an approximation is required to solve the SE. The earliest used approximation was the Hartree approximation.

3.2.1 Hartree approximation

Hartree developed a method to include the electron repulsion in the SE, while retaining some of the simple features of the independent particle model. The Hamiltonian for an \( n \)-electron atom as an independent particle model where the electron repulsion is ignored. This is shown in equation (3.5)

\[
\hat{H}^{(0)} = \sum_{i=1}^{n} \hat{H}^{(0)}_i \tag{3.5}
\]

where \( \hat{H}^{(0)}_i = -\frac{1}{2} \nabla^2_i - \frac{Z}{r_i} \) and atomic units are used (as they will be for the rest of this chapter). This shows the kinetic energy of \( i \) electrons and the potential energy due to the Coulomb interaction with the nucleus. When the sum of the electron–electron repulsion is included in the Hamiltonian then it will become equation (3.6).

\[
\hat{H} = \hat{H}^{(0)} + \sum_{i<j} \frac{1}{r_{ij}} \tag{3.6}
\]

The many body wave function equation (3.7), is now the product of \( n \) orbitals designated by \( \phi_i(i) \).

\[
\Psi(1, 2, ..., n) = \phi_1(1)\phi_2(2)\ldots\phi_n(n) = \prod_{i=1}^{n} \phi_i(i) \tag{3.7}
\]

This orbital can describe the effective potential of a single electron as shown in equation (3.8).

\[
V_i^{\text{eff}} = \sum_{j\neq i}^{n} \int \frac{\phi_j^*(j)\phi_j(j)}{r_{ij}} dv_j \tag{3.8}
\]

This simplified potential allows the individual electron coordinates to be separated in the wave function, which means the solution is of \( n \) equations (3.9).

\[
(H_i^0 + V_i^{\text{eff}})\varphi_i(i) = \epsilon_i \varphi_i(i) \tag{3.9}
\]

3.2.2 Hartree-Fock approximation

The Hartree wave function (equation (3.7)) comprises spatial orbitals of one electron. It does not satisfy the Pauli exclusion principle. The Slater wave functions (Slater determinant) consist of spin orbitals which are a combination of the spatial orbital with the
spacial orbital with a spin function \((s_i = \alpha \text{ or } \beta)\). The Slater determinant for an \(N\) electron system is shown in equation (3.10).

\[
\Psi(r_{1s_1}, r_{2s_2}, ..., r_{Ns_N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\Psi_1(r_1s_1) & \Psi_1(r_2s_2) & ... & \Psi_1(r_Ns_N) \\
\Psi_2(r_1s_1) & \Psi_2(r_2s_2) & ... & \Psi_2(r_Ns_N) \\
... & ... & ... & ...
\end{vmatrix}
\] (3.10)

This ensures there are no more than two electrons in each spacial orbital. The Slater wave function ensures the Pauli exclusion principle, which means that the electrons in the same orbital must have opposite spins. The determinant becomes zero if two rows are identical, which would represent a violation of the Pauli exclusion principle.

However the interaction of an electron is with an average electrostatic field for the electrons and nuclei. There is no electron–electron interaction. This leads to an underestimation of bond dissociation energies. Over the years there have been improvements to the Hartree-Fock method to account for electron–electron interaction, but these are usually computationally expensive.

### 3.3 Density functional theory (DFT)

DFT is used for working out the ground state energy of a structure from its electron density. The main point of DFT is that the electron energy \((E)\) of the system can be found from the electron probability density \((\rho)\). This was proven by Hohenberg and Kohn [79].

At the beginning of DFT some useful approximations were produced such as the Thomas–Fermi–Dirac model. From the wave function (equation (3.4)) comes the energy functional of equations (3.11).

\[
E(\rho) = T(\rho) + V_{Ne}(\rho) + V_{ee}(\rho)
\] (3.11)

The electron–electron repulsion \(V_{ee}\) can be broken up into two parts: Coulomb \((J(\rho))\) and exchange \((K(\rho))\).

Two of the terms in (3.11) are given by the classical terms: \(V_{Ne}(\rho)\) and \(J(\rho)\), shown in equations (3.12) (3.13).

\[
V_{Ne}(\rho) = \sum_A Z_A \int \frac{\rho(r_1)}{r_{A1}} dr_1
\] (3.12)

\[
J(\rho) = \int \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2
\] (3.13)
The other two $T(\rho)$ and $V_{Ne}(\rho)$ started using the assumption of a non-interacting uniform electron gas but this does not predict bonding.

### 3.3.1 Kohn-Sham

Kohn and Sham [80] split the kinetic functional $T(\rho)$ into two parts, the first produces an exact result, the second is a correction. The kinetic functional $T(\rho)$ for a system of non-interacting electrons can be expressed as equation (3.14).

$$T(\rho) = \sum_{i=1}^{n} \left\langle \Psi_i \left| -\frac{1}{2} \nabla_i^2 \right| \Psi_i \right\rangle$$  \hspace{1cm} (3.14)

There is only a small difference between the exact kinetic energy and what the non-interacting electron system calculated (3.14). This small difference in the kinetic energy goes into the exchange correlation term ($V_{xc}$).

Equation (3.11) expands as shown in equation (3.15).

$$E(\rho) = T(\rho) + V_{Ne}(\rho) + J(\rho) + V_{xc}(\rho)$$  \hspace{1cm} (3.15)

With the information in equation (3.12)–(3.15) expands into (3.16).

$$E(\rho) = -\frac{1}{2} \sum_{i=1}^{n} \left\langle \Psi_i \left| \nabla_i^2 \right| \Psi_i \right\rangle + \sum_{A} Z_{A}^{\rho} r_{A1} + \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 + V_{xc}(\rho)$$  \hspace{1cm} (3.16)

The exact ground state density is shown in equations (3.17), which is summed over all the occupied Kohn–Sham orbitals.

$$\rho(r) = \sum_{i=1}^{n_{occ}} |\Psi_i(r)|^2$$  \hspace{1cm} (3.17)

### 3.3.2 Exchange–correlation

There have been a few exchange–correlation approximations over time. The main source of error in DFT is from these approximations. The function $V_{xc}$ is generally split into two parts: the exchange and the correlation functions.

The calculations in this study use the local density approximation (LDA), with the exchange–correlation functional is shown in equation (3.18).

$$V_{xc} = \int \rho(r) \epsilon_{xc}[\rho(r)] dr$$  \hspace{1cm} (3.18)

Where $\epsilon_{xc}[\rho(r)]$ is the exchange-correlation energy per electron in a homogeneous electron gas. This approximation assumes that the positive and negative charges are evenly...
CHAPTER 3. AB INITIO THEORETICAL BACKGROUND

distributed. The $\epsilon_{xc}[\rho(r)]$ can be split in two, shown in equation (3.19).

$$
\epsilon_{xc}[\rho(r)] = \epsilon_x[\rho(r)] + \epsilon_c[\rho(r)]
$$

(3.19)

Where $\epsilon_x[\rho(r)]$ is the exchange energy of an electron in a uniform electron gas, as expressed in equation (3.20).

$$
\epsilon_x[\rho(r)] = -\frac{3}{4} \sqrt{\frac{3\rho(r)}{\pi}}
$$

(3.20)

The $\epsilon_c[\rho(r)]$ is the correlation energy and is calculated from Monte Carlo simulations and analytical treatments. The one used in AIMPRO was originally parameterised by Perdew and Zunger [81] and then improved later by Perdew and Wang [82]. LDA is widely regarded as a reasonable approximation with ability to predict structural properties, although it can overestimate the bonding energy.

Another approximation that is widely used today is the generalised gradient approximation (GGA). This is LDA with a gradient correction, which accounts for the inhomogeneity of the electron density. This approximation is good at calculating d-metal complexes [83].

3.3.3 Basis set

Basis sets are used in calculations to describe the unknown molecular orbitals $\Psi_i$ in equation (3.21), as a linear combination of basis functions ($\psi_s$).

$$
\Psi_i = \sum_{s=1}^{M} C_{si} \psi_s
$$

(3.21)

where $C_{si}$ is the expansion coefficient. The larger the basis set the more accurate the approximation. The most used types of basis sets are plane–waves, Slater type or Gaussian type orbitals.

For the calculations in this study Gaussian type orbitals were used. The general form for the Gaussian function is equation (3.22).

$$
\phi_{ijk}(r_1 - r_c) = (x_1 - x_c)^i(y_1 - y_c)^j(z_1 - z_c)^k e^{-\alpha|r_1 - r_c|^2}
$$

(3.22)

Where $x_c, y_c, z_c$ are Cartesian coordinates of the centre of the Gaussian function ($r_c$). The Cartesian coordinates for the electron are represented as $x_1, y_1, z_1$. The designations $i, j, k$ are positive integers that dictate the symmetry of the orbitals. For an s-type Gaussian orbital $i = j = k = 0$, p-type $i + j + k = 1$, d-type $i + j + k = 2$ and so on. In AIMPRO
the basis set comprises several different exponent ($\alpha$) values. Each value gives rise to a series of basis orbitals of different symmetry from $i + j + k = 0$ up to a maximum value (1 or 2 normally, labelled $p$ or $d$ respectively). Thus a basis of four different exponents could be labelled $pdpp$ or $dddd$, for example.

The main advantage of using Gaussian orbitals is that the product of two orbitals is the equivalent of one function that is centred between the two. This facilitates analytic integration, making the computer calculation smaller and so is not as computationally expensive as Slater type orbitals.

### 3.3.4 Pseudo-potential

The larger the basis set the more accurate the results, but also the time to solution generally goes at least as $N^3$ for $N$ basis orbitals, so further simplification is needed. This is done by using a pseudo-potential [84]. The core electrons have no effect on the bonding of the atom and are very tight on the nucleus, requiring very narrow Gaussian orbitals. The effects of the core electrons are incorporated into the nuclear potential (pseudo-potential). The valence electrons are treated separately. This reduces the computational cost significantly.

As mentioned the electron–nuclear Coulomb attraction is not needed for the core as it has no effect on the chemical environment. So the Coulomb potential for the core is replaced with a smooth pseudo–potential, an example plot is shown in Figure 3.1. This represents the Coulombic force outside of the core and the combination of this with the

![Figure 3.1: Plots from Hasnip et al. paper on DFT on solid state [85]. The first plot shows the Coulomb potential in the dashed line and the solid line is the pseudo-potential for C. The second plot shows the wave function for 2s–orbital.](image-url)
requirement on valence wave functions to be orthogonal with core wave functions inside the core. The second plot in Figure 3.1 shows the 2s–orbital and the pseudo–wave function.

The improvement of pseudo-potentials over time has been a focus of many studies, and there are a variety that are available [86]. Originally the AIMPRO package used the pseudo-potential created by Bachelet et al. [87] which was for hydrogen (H) to plutonium (Pu). The pseudo-potential currently used in the AIMPRO package was developed by Hartwigs et al. [88]. They produced Gaussian pseudo-potentials from hydrogen (H) to radon (Rn).

3.3.5 Geometry optimisation

Geometry optimisation, optimises the structure to the minimum in the potential energy surface (stable geometry). The AIMPRO package uses the conjugate gradient method which is based on the steepest descent method that was also used in EDIP.

How this package optimises is summarised in the flow diagram in Figure 3.2. This begins by calculating the total energy and the forces. Then a search direction is generated: for the first stage this is just the direction of force on each atom, then for the iterations after that the conjugate direction is chosen (a direction which is orthogonal to the previous one). The atom is then displaced along that direction until a minimum in energy is reached whereupon a new energy and direction are calculated. This is repeated until the change in structure and energy are small enough. In this work, the conjugate gradients iterations stopped when forces (or even changes between iterations) fell below the default value of $1.05 \times 10^{-5}$ Au. The resulting geometry is generally the nearest local minimum in energy.

3.4 Ab Initio Modelling Program (AIMPRO)

As mentioned earlier in this chapter the total energies of model defects in supercells are calculated using the AIMPRO package [89, 90], which is based on density functional theory (DFT). AIMPRO was started in the late 1980’s in Exeter and is one of the oldest DFT codes in Britain [91].

This package describes the ground state properties in terms of the electron density distribution. Many options are available in the AIMPRO package: however, in this case the local density approximation (LDA) within DFT, according to the formula by Perdew and Wang (PW92) [82], was used to calculate the exchange-correlation component of the
total energy. A basis set of Gaussian orbitals is used to represent the wave function of the valence electrons, in this case ppdp was used. The electron density is expanded as plane waves with a maximum kinetic energy of 248.8 Hartrees. The pseudopotential is based on the Hartwigsen-Goedecker-Hutter (HGH-pots) scheme, and is used to represent the core electrons. The Monkhorst-Pack method [92] is used to sample the band structure, with the Methfessel-Paxton scheme for occupying the Kohn-Sham levels. An analytical formula derived from the total energy expression is used to calculate the forces used for structural optimization.
3.4.1 Filtration

In 2009 the filtration method was added to the package which allows for a larger number of atoms in the system with a smaller computational cost \cite{93}. In this method, the DFT problem is solved for the local environment around each atom. The resulting occupied and some user-defined unoccupied wavefunctions are then used, after some numerical treatment, as basis functions. Since typically only four such filtered basis functions per atom are needed, the speed of the code is enormously enhanced compared with the full basis, but since the basis is tuned to each atomic environment there is no meaningful compromise in precision.
Chapter 4

MD simulation of irradiation damage of graphite

As mentioned in the introduction (Chapter 1) there are different physical processes which were shown in Figure 1.4. These processes are represented in different types of simulations previously shown in Figure 1.5. So this chapter will consider each different physical process in turn.

4.1 Introduction

The three different types of simulation in this chapter represent the principal damage produced in the reactor. The first section is about the thermal spike which examines the swift heavy ion regime. The next section relates to the cascade regime which includes the threshold displacement energy. The final section concerns different defects’ energies which helps to validate the decision to use of EDIP.

4.2 Thermal spike

The thermal spike simulation represents the carbon atoms at the highest energy range. This is the swift heavy ion region, which is where the carbon atom has an energy so large that they lose their energy via the electrons. So as the carbon atom travels through the graphite it loses energy via the interaction of it’s electrons and the electrons of the surrounding carbon atoms in the graphite.

Thermal spike effects are known to be important in metals and oxides [23], but are
thought to be unimportant in graphite [94]. Atomistic potentials such as EDIP do not contain the physics of electron interaction. Nevertheless, if the PKA deposits energy in the electron system and this then equilibrates with the nuclear system, the result will be a thermally excited region around the path of the PKA. This region is what is simulated here, assuming it is cylindrical and given a certain energy deposition rate per unit length of path.

4.2.1 Method

Using the method for simulating the thermal spike described in section 2.5, these simulations were performed at an initial temperature of absolute zero, room temperature and the upper limit of the AGR’s (i.e., 0 K, 300 K, and 900 K). These temperatures are achieved by thermal equilibration. All the simulations in this section use periodic boundary conditions (mentioned in Section 2.1.4). The simulations of the thermal spike assume a cylindrical region with a range of radii and a range of kinetic energies given to the atoms in the spike region.

The \( \frac{dE}{dx} \) were chosen to represent a PKA from a neutron at the most realistic energies seen in a nuclear reaction. Given the neutron energy spectrum in Chapter 1 in Figure 1.2 the most common neutron energy produced is between 1 – 2 MeV, for an example of how the \( \frac{dE}{dx} \) was calculated by taking a common neutron energy of 1 MeV.

Neutron energy = 1 MeV
15% transferred to carbon = 150 keV
Per nucleon = 12.5 keV

So when 0.0125 MeV is read off the graph in Figure 4.1 this will give an electronic stopping power (ESP) of \( \sim 2 \text{ MeV}/(\text{mg/cm}^2) \). The \( \frac{dE}{dx} \) in the graphite is worked out as follows:

\[
ESP \times \rho \simeq 4740 \text{ MeV/cm}
\]
\[
\simeq 47.4 \text{ eV/Å}
\]

Where we take the density of graphite (\( \rho \)) in the simulations to be 2370 mg/cc. With a quarter of that energy going into nuclear motion, we obtain:

\[
\frac{dE}{dx} \simeq 12 \text{ eV/Å}
\]

Taking three examples of different energy thermal spike simulations, the first two show the range of the most common neutrons: 1 MeV (\( \frac{dE}{dx} \simeq 12 \text{ eV/Å} \)) and 2 MeV
The third example is at the higher energy range of the neutrons which is less likely to be seen in the nuclear reactor of 6 MeV ($\frac{dE}{dx} \approx 37 \text{ eV/Å}$). These three simulations are shown in Figure 4.2 are equilibrated at 300 K and consist of 3840 atoms.

The snapshots of the simulations show the evolution of the spike, starting at 0.04 ps (top row) which is the point of the simulation with the highest energy and ending at 1.67 ps (bottom row) which is the time when the structure has stabilised. The time frame for these simulations is short due to the quick dispersion of the energy entered into the system. The energy going into each atom in the spikes shown is 2 eV per atom, but the radius is increased to represent the three different $\frac{dE}{dx}$ values seen in Figure 4.2, where the radius goes from 4.0 Å, 5.2 Å and 7.2 Å from left to right.

4.2.2 Results

Time evolution

The time evolution of the thermal spike in graphite was shown in Figure 4.2 of the structures at the beginning and the end of the simulation. Another way to represent this is to look at the temperature of the simulation as a function of time. The plot in Figure 4.3 represents temperature versus time of the three $\frac{dE}{dx}$ cases. This plot shows the spike in terms
of temperature (energy) going into the system and how it is lost. The spike corresponding to typical fission neutrons (1–2 MeV) dissipate quickly without leaving any defects. The outlying neutron energy (6 MeV) gives a spike which endures longer and leaves defects.

The structure was equilibrated at 300 K but the plot (Figure 4.3) only goes down to 400 K and this could be due to the Berendsen thermostat, as implemented as a boundary
thermostat in the EDIP code. This thermostat does not remove the additional energy from the system as realistically as possible, resulting in an increased temperature [96]. Usually the choice of thermostat and its parameters is justified by using a strictly equilibrium approach and describing the NVT ensemble. When the simulation is non-equilibrium i.e. when kinetic energy is added to the system, such as the thermal spike the effective removal of the energy at the boundaries of the cell become more critical in order to correctly control the temperature. A more realistic approach is to use the generalized Langevin equation as implemented in stochastic boundary conditions [96] to correctly account for the coupling of the simulation cell boundaries to the infinite crystal heat bath, which has been successfully applied in other MD simulations of irradiation defect formation [97]. The damping constant must be correctly calibrated to reproduce the transfer of kinetic energy at the boundaries of the cell. This can be done using the MD simulation set-up to determine the phonon density of states via the velocity auto-correlation function of atoms in the central region and finding the damping constant that best matches with the analytical lattice phonon density of states [98]. Although this would improve the long-timescale behaviour of this simulation, in this case the boundary thermostat has negligible effect on the results since the system is large enough that all the structural changes occur before the additional kinetic energy dissipating from the PKA reaches the simulation cell boundaries.

**Damage**

Thermal spikes in graphite at the lower \(\frac{dE}{dx}\) produce no defects at the end of the thermal spike simulation (when it has stabilised). At this lower end of the energy scale the graphite manages to completely repair itself. Then at the intermediate \(\frac{dE}{dx}\) there are only a few defects seen at the end of the simulations. It is only at the highest \(\frac{dE}{dx}\) that damage is really seen at the end of the simulations. This shows how resilient the graphite is even for the less likely events of higher energy neutron. An example of the higher energy \((\frac{dE}{dx} = 37\ \text{eV/Å})\) thermal spike result can be seen in Figure 4.4. On the left in Figure 4.4(a) where a large radius and lower amount of energy is going into each atom, no real defects are produced. The defects seen are artefacts of the potential which is the sp\(^3\)--sp\(^3\) cross-link, this defect will be discussed in more detail later on in Chapter 4.4. Then on the right in Figure 4.4(b) which has a smaller radius and more energy into each atom damage is seen.
Even though there are very few defects produced in most of the simulations, it is only at the higher energy range with the higher density (low radius with high energy per atom) that really produces significant numbers of defects. The Table 4.1 shows the number of defects produced at different $\frac{dE}{dx}$ and the energies going into each atom in the thermal spike. In the lower energy simulations there are no defects produced, only the linking defect are seen at the end of the simulation. It is only at the $\frac{dE}{dx} > 30$ eV/Å that we see a production of defects such as interstitials, vacancies which make up the FP defects. Also seen at the end are the Dienes defect. More are seen when there is a higher concentration of energy in the thermal spike.

At the 0 K thermal spike simulations more defects are seen at the end of the simulations compared to the higher temperatures. This is due to the fact that the surrounding atoms have no vibration which means that defects are not relaxing when compared to the simulations that have a temperature. There is also a difference in the number of defects between 300 K and 900 K as the higher temperature is producing more defects, due to the extra energy.

In Figure 4.5 there is an example of the defects mentioned; the red atoms are highlighting the interstitial and the blue represents the vacancies. The gold shows pentagons, which makes locating the Dienes defect easier to locate in the larger structures. When the number of defects are counted at the end of each simulation the $sp^3–sp^3$ cross-link defect
Table 4.1: The number of defects formed in the thermal spike simulation at different temperatures. The count was done after quenching and the linked defect does not count as a defect, only Frenkel pairs and the Dienes defects were recorded.

<table>
<thead>
<tr>
<th>$E_{\text{atom}}$ (eV)</th>
<th>$\frac{dE}{dx}$ (eV/Å)</th>
<th>$T = 0$ K</th>
<th>$T = 300$ K</th>
<th>$T = 900$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>35</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>35</td>
<td>60</td>
<td>0</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 4.5: Diagram of the structure after a thermal spike at $T = 300$ K with 4 eV of energy going into each atom to produce a spike of $\frac{dE}{dx} = 35$ eV/Å. The red atoms represent interstitials and blue are vacancies, with the gold lines showing pentagons to highlight the Dienes defect.

was not included in the count. This meant that at the end of each simulations the defects had to be counted by eye.
These simulations are performed in the small structures (3840 atoms) this is so that the damage can be easily counted. When there are larger structures this is not possible so instead a custom code by T. Trevethan [99] is used which finds the vacancies (blue atoms) and the interstitials (red atoms). The code compares the starting structure with the final structure and produces two outputs: the first being the vacancies which are when an atom is not within the cutoff $r = 1.0 \, \text{Å}$ of a lattice site. The second is the interstitials which are when there is no reference point within $r = 1.0 \, \text{Å}$ of the atom in the final structure. Even harder to see is when a Dienes is formed so again another custom code by T. Trevethan [99] is used which finds polygons in the structure. This is done by looking at the $xyz$ coordinates of the final structure in the simulation and finding all the three body, four body and five body that have formed within the bond length tolerance. Then an output which is shown in red in the Figure 4.6. In Figure 4.5 these polygons are highlighted in gold.

When the energy per atom is high (4 eV per atom) it also produces more defects compared to the lower energy 3 eV per atom. This is due to the higher density of energy. An attempt to improve the simulation of a thermal spike in graphite was attempted, where we expect the energy to be more intense at the centre with a lower energy density at the edge of the cylinder (energy density tapers off at the edge). Thus is described below as a ‘Gradual Spike’.

**Temperature**

Initial temperature has very little affect on the simulations, it is only when you start a simulation at absolute zero that a difference is really seen. A comparison on temperature
can be seen in the three plots in Figure 4.7. The plots are for the simulations at 0 K in

Figure 4.7: Plot of number of defects (FP and D) produced in thermal spike simulations with different $\frac{dE}{dx}$. The different plots are from different equilibration temperatures where (a) is at 0 K with the trends $y(x) = 0$ (blue), $y(x) = 0.133x - 0.812$ (blue) and $y(x) = 3.455x - 66.090$ (green). (b) is at 300 K with the trends $y(x) = 0$ (blue), $y(x) = 0.448x - 9.457$ (red) and $y(x) = 0.969x - 15.390$ (green). (c) is at 900 K with the trends $y(x) = 0$ (blue), $y(x) = 0.067x + 0.594$ (red) and $y(x) = 1.515x - 25.300$ (green).
Figure 4.7(a), 300 K in Figure 4.7(b) and 900 K in Figure 4.7(a).

The data here is probably too limited to draw concrete conclusions, but the following is possible: At the highest chosen energy ($E$) per atom (4 eV) the threshold lies between 15 and 20 eV for all temperatures, while defect generation after the threshold occurs at rates between 4 defects Å/eV (0 K) and 1 defect Å/eV (300 K). At the energy per atom 2 eV the threshold is not met, and at the energy per atom 3 eV the threshold is poorly determined (anywhere between 0 and 20 eV) and defect generation is low (0.1 to 0.5 defects Å/eV).

The 0 K plot has a higher number of defects produced at the end of the simulation compared to the other two temperatures plotted. This could be due to the fact that the atoms at a finite temperature are vibrating enough to heal some of the defects.

When the 300 K and the 900 K simulations are compared there is not as large a difference between the two compared to the 0 K. The higher temperature in this case produces a higher number of defects than the other, which would be expected as the extra energy here will mean the interstitials and vacancies are further apart.

**Gradual spike**

To represent a more realistic thermal spike in graphite the cylinder can not just have atoms with the same energy, but the energy needs to gradually get lower. This means the atoms at the centre will have a higher energy than those at the edge of the cylinder. This is shown in Figure 4.8 which shows the higher energy at the centre of the cylinder by the white and as the energy goes down it goes to red. For the thermal spike of $\frac{dE}{dx} = 12$ eV/Å.
the Table 4.2 shows how much energy goes into each atom in the different annular region.

<table>
<thead>
<tr>
<th>Radius of spike (Å)</th>
<th>Energy per atom (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>16</td>
</tr>
<tr>
<td>2.0</td>
<td>8</td>
</tr>
<tr>
<td>2.5</td>
<td>6</td>
</tr>
<tr>
<td>3.0</td>
<td>4</td>
</tr>
<tr>
<td>3.5</td>
<td>3</td>
</tr>
<tr>
<td>4.0</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4.2: This is for a thermal spike of $\frac{dE}{dx} = 12$ eV/Å showing the energy going into the atoms in the different annular regions. With a higher energy at the centre and dissipating to the edges.

These types of thermal spike create more damage than in the spike with all the atoms having the same energy. This is shown clearly in Figure 4.9, which has a low $\frac{dE}{dx}$ of 6 eV/Å,

Figure 4.9: The structure of the graphite after a gradual thermal spike of power $\frac{dE}{dx} = 6$ eV/Å at 300 K. The red atoms represent the interstitials, the blue atoms represent the vacancies and the gold highlights the polygons.
but produce the same amount of damage as the high energy thermal spike. More damage is produced due to the fact that there is more energy going into the system, as there the centre of the cylinder will get more and more energy.

**Graphite comparison**

For a comparison of how graphite reacts in these simulations other materials were simulated. Only carbon structures can be simulated using EDIP. The structures used for comparison in this section are diamond and different density amorphous carbons that were provided by N. Marks. The latter were created by cooling gaseous carbon of different temperatures [100, 101].

A thermal spike in diamond given the same spike radius and the same energy per atoms in the cylinder produces a higher $\frac{dE}{dx}$ value than graphite with the same parameters. This is due to diamond having a higher density in the simulation of 3.498 g/cc than graphite with a density of 2.375 g/cc.

When the spike is put through diamond you can see the atoms move in a wave as the energy travels out from the spike. This is clearly seen in the time intervals in Figure 4.10, with the spike being clearer from the side in diamond compared to graphite. Another clear difference is that diamond recovers more quickly than graphite which could be due to the rigidity and the higher isotropic thermal conductivity. It is only at the higher energies that any defects are seen at the end of the simulations. The only defect seen in these simulations is the bond swap defect [102, 103] (which could be thought of as a 3D analogue of the Dienes defect), shown in Figure 4.11. The defect in the diamond structure first appeared in the construction of models of amorphous silicon thirty years ago [104] and in simulations of melting [105].

The amorphous carbon structures [106, 101] that are used in the simulations have different densities. The three densities used are 1.5 g/cc, 2.0 g/cc and 3.0 g/cc. The low density amorphous carbon is glassy carbon shown in Figure 4.12(a) and then there is high density carbon in Figure 4.12(b). The glassy carbon has sheets of graphene that are rippled, whereas the high density does not have any clear structure. Another way to look at the structures is with the percentage of types of bonding. When the structures have been equilibrated at room temperature 300 K the percentages of the bonds are shown in Table 4.3. This shows that the low density glassy carbon is most like graphite which has
When a thermal spike simulation is set up with a width of 5.8 Å and an energy of 3 eV going into each atom, this will produce a different thermal spike dependent on the density of the structure. Graphite with a density of 2.375 g/cc will have a thermal spike stopping power of $\frac{dE}{dx} = 36.7$ and the amorphous graphite 1.5 g/cc will experience a stopping power $sp^2$ bonds.
Figure 4.12: Amorphous carbon \cite{100, 101} (a) has a density of 1.5 g/cc and (b) has a density of 3.0 g/cc.

\begin{table}[h]
\centering
\begin{tabular}{llll}
Density & sp\(^1\) & sp\(^2\) & sp\(^3\) \\
(g/cc) & (%) & (%) & (%) \\
\hline
1.5 & 3.1 & 90.1 & 6.8 \\
2.0 & 19.4 & 64.5 & 16.2 \\
3.0 & 1.2 & 48.3 & 50.5 \\
\hline
\end{tabular}
\caption{Amorphous carbon \cite{100, 101} and the percentage of the types of bond in the structure after equilibration of 300 K.}
\end{table}

of \( \frac{dE}{dx} = 23.2 \), 2.0 g/cc will have a power of \( \frac{dE}{dx} = 31.5 \) and 3.0 g/cc will have a power of \( \frac{dE}{dx} = 48.9 \). When the thermal spike travels through the structures it will affect the bonding in the structures which can be seen in the plots in Figure 4.13. This show the percentage of sp\(^1\), sp\(^2\) sp\(^3\) in the different density amorphous carbon during the thermal spike. With the glassy carbon and the low energy there is little change in the structure (Figure 4.13(a)), which matches the results seen in the graphite although a \( \sim 0.5 \) % shift from sp\(^1\) to sp\(^2\) content indicates a slight improvement in order. Whereas the other two amorphous structures see more of a change during the simulations. This is highlighted in Figure 4.13(b) where it appears that sp\(^1\) fraction decreases by \( \sim 3 \) %, while sp\(^2\) and sp\(^3\) increases by 1-2 %. In Figure 4.13(c) none of these changes can be described as profound or as a phase change, such as crystallisation, but could indicate an improvement in order.
Figure 4.13: Plots of the percentage of types of bond during a thermal spike in amorphous carbon at 300 K. Where (a) density is 1.5 g/cc, (b) density is 2.0 g/cc and (c) density is 3.0 g/cc. The blue line is the sp bonds, the red line is the sp$^2$ bonds and the green line is the sp$^3$ bonds.
Healing defects

In the literature it is seen that the thermal spike is able to heal defects in semiconductors. One such paper is by Backman [107], where he ran MD simulations on SiC and observed the healing of defects in the swift heavy ion region. This has also been seen experimentally in Dunlop et al. [108] where the graphite has a rapid recovery of the disorder created by the heavy ion irradiation. So this section will look at defected graphite and what happens to the defect after a thermal spike has travelled through the defected area.

These simulations are the same as the other thermal spikes except that there is a defect in the starting structure. The defect was optimised in a structure large enough that the periodic boundary would not effect the thermal spike simulation. This requires a starting temperature at 0 K. The thermal spikes could not be simulated at an equilibration temperature of 300K due to the fact that this moves the defect. Consequently the only energy going into the system is from the thermal spike.

The first defect is the flat reconstructed vacancy, in the $\alpha$ and $\beta$ positions. Looking at the higher energy spikes of $\frac{dE}{dx} = 36.7$ eV/Å, there is movement of the vacancy as seen in Figure 4.14, which shows the original defect of the $\alpha$ single vacancy in Figure 4.14(a) with red arrows showing the movement of the atoms in the thermal spike simulation. One of the arrows shows the atom moving up into the vacancy space, and the other arrow shows another atom moving across to fill the space that has just been created by the first atoms.

![Figure 4.14](image)

Figure 4.14: Thermal spike simulated through an $\alpha$ single vacancy at the high energy of 36 eV/Å, where (a) is the single vacancy with arrows showing the direction the atoms move during the simulation. (b) is the single vacancy’s new position after the simulation.
movement. The new position of the vacancy at the end of the simulations is shown in Figure 4.14(b). The vacancy does not always move even at the high energy, but a larger defect can be formed around the original defect which is shown in Figure 4.15. After

\[ \text{Figure 4.15: Thermal spike through a } \beta \text{ single vacancy at the high energy of 36 eV/Å.} \]

(a) and (b) show only the layer of the initial vacancy, whereas (c) includes a neighbouring layer.

the simulation a larger defect was formed around the $\beta$ single vacancy in Figure 4.15(a). When just looking at the layer of the original defect it appears to have produced a vacancy loop (Figure 4.15(b)) but this is an artefact of the window used to view a single layer. When you look sideways including a neighbour layer (Figure 4.15(c)) you can see a ramp is created linking the two layers so the vacancy has been converted into a locally amorphous region.

Now looking at what happens to the lowest energy and most stable of interstitials (spiro Figure 1.7(a)) in the thermal spike at this high energy. At the spike of $\frac{dE}{dx} = 21 \text{ eV/Å}$ the interstitial does not move and again it is only at the higher energy range $\frac{dE}{dx} = 36 \text{ eV/Å}$ that there is any movement of the defect. This movement is highlighted in Figure 4.16. The initial structure of the single interstitial is shown in Figure 4.16(a) with the red arrows showing the motion of the atoms as the interstitial moves down and creates the new defect seen in Figure 4.16(b). The interstitial has knocked a neighbouring lattice atom out of its
site, creating a vacancy and di-interstitial in the neighbouring interlayer space.

The vacancy and the interstitial in these examples do not heal. This is due to the fact that each structure has either a missing atom or an extra atom, so there is nowhere for the defect to heal. For healing to be seen in a thermal spike the best example will be from the Frenkel pair.

An intimate FP when equilibrated at 0 K was found to heal when the vacancy is the nearest neighbour atom to the interstitial. Thus for these simulations the vacancy and interstitial will need to be separated when starting the thermal spike simulations. An example of the starting structure can be see in Figure 4.17. During this equilibration the interstitial is already on the way back to healing the vacancy below. So with the thermal spike it will only take a small amount of extra energy to heal this defect. With $\frac{dE}{dx} = 10 \text{ eV/Å}$ the damaged graphite is healed. Just as the case of perfect graphite at the end of the simulations there remain only a few of the linking defects, which we dismiss as artefacts of EDIP as will be discussed later in section 4.4.2.

When the vacancy and interstitial are separated by a layer of graphene, then the defect does not heal. At the high energy $\frac{dE}{dx} = 36 \text{ eV Å}$ the interstitial has moved across several layers, but has not healed the vacancy.

4.2.3 Discussion

The first thing to note is that these simulations attempt to reproduce a thermal spike by imposing a pseudo-random set of initial atomic velocities equivalent to what should result from the energy deposited by the electronic stopping power. Here we have only one sim-
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55

Figure 4.17: Starting structure of an intimate Frenkel pair equilibrated at 300 K. The first image is a top view and the second is with a side view.

ulation at each temperature, whereas ideally there should be an ensemble of simulations, each with different initial velocities that also give the stated electronic stopping power. The discussion here is to be read with this in mind.

The thermal spike simulations transfer a great deal of energy into the graphite and produce very little damage. It is only at the higher end of the energy range of the neutron energy transfer to a carbon atom that any real damage is produced in the graphite structure. The higher number of defects are being produced when the radius of the spike is smaller and higher energy given to each atom. Looking at the most likely neutron energy that is seen in a nuclear reactor the thermal spikes have made little to no change from the initial structure. It is only the link defect that is seen at the lower energy range and this is an artefact of the code and would not be created in the graphite. The Dienes defect is seen presumably by direct thermal activation, although in the cascade simulations it is the product from the collapse of an intimate Frenkel pair.

When looking at the temperature of the simulations more damage is seen in the 0 K simulations as the graphite does not have the vibrational energy to remove any instantaneously formed defects. Whereas the simulations at a finite temperature allow a degree of defect removal so will produce fewer defects. The 600-900 K simulations represent what
is happening in the nuclear reactor. The comparison of the structures at the end of the simulations done at room temperature (300 K) are very similar to the simulations done at high temperatures (900 K).

With the simulation performed using the gradual spike there are regions of higher energy density so more damage is seen when compared to the original spike. This type of simulation would have been better if the code allowed different energies going into the atoms in the cylinder and as such is not a clear representation of a true thermal spike. This could be carried on for future work to produce a more realistic simulation.

When comparing graphite with the other carbon structures it is clear that graphite is least likely to be affected by the thermal spike. When compared to the diamond simulations in which the wave is clearly seen travelling through the structure this is not seen in graphite. Like graphite the diamond structure only sees defects at the end of the simulation at the higher end of the energy. Glassy carbon with its more layered nature it acts most like graphite. Just like graphite it can absorb the energy with very little change from the initial structure.

These thermal spikes in the graphite have the possibility for healing defects and at the high energy thermal spikes all the defects become mobile. The intimate FP collapses before the simulation and when they are further apart there is motion but they do not heal, in the case studied. Graphite in the nuclear reactor will have more defects so will have more sites for the interstitials to heal to. This makes it more likely that the damage in the graphite will be healed by the PKA’s.

4.3 Cascade

The cascade simulations show the path of a carbon atom as it is displaced from its original site and the way it travels through the graphite. Also seen during these simulation is the type of damage that is created and healed.

These simulations have various PKA energies. The top range for the PKA energy is at $\sim 2$ keV. This cap is due to the fact that a larger PKA energy will require a larger cell structure. The lower PKA energy range goes down to the TDE range (20–100) eV. The TDE is the lowest energy required to create a Frenkel pair defect.

There has not been much published for cascade simulations in graphite, the main simulations that have been done are focused on the TDE of graphite. There is some ambiguity
in literature on this value, which ranges from 10-60 eV. The TDE paper authored by myself addresses the issue in more detail about previous literature on TDE so far [99]. The Table 4.4 is from this paper and shows the previous values found. This table shows that there seems to be an effect on the value when the temperature of the system is changed

<table>
<thead>
<tr>
<th>author</th>
<th>method</th>
<th>(E_d) (eV)</th>
<th>notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eggen et al. [109]</td>
<td>electron bombardment</td>
<td>24.7 ± 0.9</td>
<td>@ 290K</td>
</tr>
<tr>
<td>(1950)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lucas et al. [110]</td>
<td>electron irradiation</td>
<td>60 ± 10</td>
<td></td>
</tr>
<tr>
<td>(1963)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montet [111]</td>
<td>electron irradiation</td>
<td>33 ± 1</td>
<td>(0–60)°</td>
</tr>
<tr>
<td>(1967)</td>
<td></td>
<td>60</td>
<td>80°</td>
</tr>
<tr>
<td>Montet [112]</td>
<td>electron irradiation</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>(1970)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ohr et al. [42]</td>
<td>electron irradiation</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>(1972)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nakai et al. [113]</td>
<td>He(^{+}), Ar(^{-}), Xe(^{+}) irradiation</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>(1991)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marton et al. [114]</td>
<td>noble–gas ions irradiation</td>
<td>34.5 ± 1</td>
<td></td>
</tr>
<tr>
<td>(1993)</td>
<td>&amp; CHARMM simulation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smith et al. [64]</td>
<td>carbon and ion bombardment</td>
<td>34.0</td>
<td>AA stacking</td>
</tr>
<tr>
<td>(1996)</td>
<td>Tersoff &amp; Brenner MD simulation</td>
<td>34.5</td>
<td>AB stacking</td>
</tr>
<tr>
<td>Zaiser et al. [115]</td>
<td>electron irradiation</td>
<td>10 – 20</td>
<td></td>
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<tr>
<td>(1997)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Banhart [116]</td>
<td>literature review</td>
<td>24 – 60</td>
<td></td>
</tr>
<tr>
<td>(1999)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hehr et al. [117]</td>
<td>carbon knock-on collision</td>
<td>44.5</td>
<td>@ 300K</td>
</tr>
<tr>
<td>(2007)</td>
<td>REBO MD simulation</td>
<td>42.0</td>
<td>@ 1800K</td>
</tr>
<tr>
<td>Yazyev et al. [31]</td>
<td>carbon knock-on collision</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>(2007)</td>
<td><em>ab initio</em> MD simulation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: The different values for the threshold displacement energy published from experimental results and simulations on irradiated graphite (from my paper [99].
and also the direction also has an impact of the value calculated.

Before explicit computer modelling of displacement, Kinchin–Pease [118] produced a formula for the number of defects \( N_d \) produced by a PKA of energy \( E \), shown in equation (4.1).

\[
N_d = \begin{cases} 
0 & 0 < E < E_d \\
1 & E_d < E < 2E_d \\
\frac{E}{2E_d} & 2E_d < E < E_1 \\
\frac{E_1}{2E_d} & E_1 < E < \infty 
\end{cases}
\]  

(4.1)

which shows the number of defects \( N_d \) is zero until the TDE \( E_d \) is reached. \( E_1 \) is the energy of the PKA when the displacement damage is saturated, i.e. 8–11 keV [119]. Then when the energy reaches twice the TDE \( 2E_d \) then the function changes. This equation is plotted in Figure 4.18(a). The Kinchin–Pease model shows that the TDE is \( E_d = \frac{E}{2N_d} \) from equation (4.1). Other early models include the Thompson Wright model of Figure 4.18(b) [120].

The method used to calculate the value for \( E_d \) has changed over time. Now a modified version of Kinchin–Pease which takes into account the displacement efficiency \( \kappa \) shown in equation (4.2).

\[
E_d = \frac{\kappa E}{2N_d}
\]  

(4.2)

Where the value for \( \kappa \approx 0.8 \), was shown by Robinson and Torrens [122] to be a constant that is independent of energy, temperature and the target material. The whole method is summarised by Norgett et al. [123] on how to calculate the number of atomic displacements generated by displaced atoms of a given energy.

4.3.1 Method

Using the method described in Section 2.5 to perform the cascades in graphite, these simulations were equilibrated at various temperatures, the same as the thermal spike simulations. Once the system is equilibrated at a required temperature then an atom (PKA) is given kinetic energy and direction. This can be seen in the plot in Figure 4.19, where blue is the equilibration period and red is the cascade period of the simulations. This plot shows the equilibration with a temperature of 300 K (blue) and then a spike in temperature when energy is given to the PKA (red). Just like the plot in Figure 4.3 the temperature does not go down to 300 K which is likely due to the thermostat.
The PKA in these cascade simulations are sent in different directions through the graphite. The code allows the input to be in Cartesian coordinates \((x, y, z)\), which can be converted to spherical polar coordinates \((\theta, \phi)\). These angles are defined in relation to the graphite structure in Figure 4.20.

An example of the PKA being set off in different directions is shown in Figure 4.21, where Figure 4.21(a) shows an example of the PKA travelling in a near prismatic direction. This shows the atoms trajectory as it travels up through the layers, creating point defects as it goes. Figure 4.21(b) shows the PKA sent in a more basal direction, in this case the
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Figure 4.19: Plot showing the complete time for a simulation including the equilibration in blue and the cascade in red. The example given here is for a cell of 112320 atoms from the 300 K equilibration and the cascade is with a PKA of 1 keV in the direction of $\theta = 55^\circ$, $\phi = 45^\circ < 1 1 3 >$.

PKA bouncing between the layers creating branches of cascades. The two simulations in Figure 4.21 shows clearly the cascades are dependent on the direction of the first displaced carbon atom. This means a varied sample of directions are required to be simulated to show the whole story.
4.3.2 Results

Time evolution

The time evolution of the cascade in graphite is shown in the plot in Figure 4.22 for three different energy cascades, equilibrated at approximately 300 K. The initial spike in energy is a lot smaller than the thermal spike as there is a huge difference in the amount of energy
going into the sample. The shapes of the plots however are similar this is due to the energy
that is added to the system at the beginning and is lost as the simulation is run.

The difference in the final temperature may be due to the approximate nature of the
rescaling process which is claimed [66] to be within 13 % of the target temperature. A
quick check on the final potential energy of these cascades gives $-962.8$ eV, $-643.5$ eV and
$-128.8$ eV for the PKA energies $2$ keV, $1$ keV and $100$ eV cases, respectively compares
with perfect $AB$ stacked graphite. These energies arise from defect creation and represent
the ‘stored’ or ‘Wigner’ energy.

**Damage**

Different types of defects are formed at the end of the simulations, the types seen in the
simulations and what they look like will be shown in more detail in Section 4.4.

The damage in these simulations is not just caused by the PKA (the atom given an
energy) but also by the secondary knock-on atom (SKA) or the tertiary knock-on atom
(TKA) and so on. An example of the damage caused in the cascades can be seen in
Figure 4.23. The figures are the quenched structures, so that the defects can be seen
clearly as quenching removes the vibration from the graphene sheets. These simulations
show the different damages seen from the change in direction of the PKA. In all the
cascade simulations various point defects are produced such as the Dienes defect, vacancies,
divacancies and interstitials.

The path of the PKA in Figure 4.23(a) travels up through the layers, with the SKA
branching off. Then in Figure 4.23(b) the PKA path is bouncing between two layers
creating branches travelling through the layers. This figure most resembles the theoretical
trajectory shown in Figure 1.4. Both these figures highlight again how directionally
dependent these simulations are.

The type of damage and when it is formed is given in Figure 4.23. At the end of the
trajectory where the energy that is available for displacement is least intimate Frenkel
pairs are most likely to be created. At the beginning of the trajectory, the defects are
more likely to be spread out. Vacancies are visualised by placing a blue sphere on their
sites, as identified by the custom code described in section 4.2.2. Generally, the vacancy
site the PKA has vacated is at one extreme of the cascade.
Figure 4.23: A cascade where the PKA energy is 1 keV at 300 K and direction (a) $\theta = 25^\circ$, $\phi = 45^\circ < 1 1 3 >$ and (b) $\theta = 72^\circ$, $\phi = 18^\circ < 3 1 1 >$. The interstitials are highlighted in red and the vacancies in blue. The path of the PKA and SKA are also shown.

Vacancies

One way to look at the damage is by examining the spread of the vacancies through the cascade simulations. In this case the focus is on the cascade simulations with a PKA energy of 1 keV in 12 different directions. The cascades were performed at 300 K and after the cascade the structures were relaxed at the end of the simulations back to 0 K. The vacancies that were formed in the simulation are counted and given a number depending on when they were formed. So 1 would be the site that the PKA vacated. As the carbon atoms are knocked out and remain out, they give rise to vacancies that are then given consecutive numbers. This can be seen in the two examples in Figure 4.24. The number
of vacancies in each simulation varies between 8 and 15. In Figure 4.24(a) there were 9 vacancies formed and in Figure 4.24(b) there were 15 vacancies. Although these are 3D cascades shown in projection, the following appears to be true (and has been confirmed by viewing in 3D): (a) vacancies are often created close to each other in neighbouring layers (such as 3 and 4 in figure 4.24(b)) and (b) in-plane divacancies also occur (such as 2 and 3 in figure 4.24(a)). The relative positioning of the vacancies could be important, because they are known to be able to bond to each other across the interlayer gap [41].

Looking at each vacancy and finding the distance between it and its nearest vacancy, we get the data given in Table 4.5 which gives averages as well as the maximum and minimum distances. Generally there is a larger range of distances between nearest neighbour vacancies for the vacancies that are created at the beginning of the cascade. For a clearer view of the data they have been plotted in the graphs in Figure 4.25. The first plot in Figure 4.25(a) shows the average distance of each vacancy to the nearest other one, and the standard deviation range is also shown. The first point has the highest average: as is to be expected since this vacancy is the PKA site. The trend is descending so at the end of the trajectory the vacancies are closer together, which is clear in the images of Figure 4.24. The second plot in Figure 4.25(b) shows all the distances for each vacancy. At the end of range for the cascades there are no large gaps between vacancies.

For the extended defects such as the ramp defect mention previously in Chapter 1.4.2
Table 4.5: The average distance to the nearest neighbour vacancy for each vacancy in each 12 different simulations. With the maximum and minimum distance between a vacancy and its nearest vacancy.

<table>
<thead>
<tr>
<th>Vacancy No.</th>
<th>Av.</th>
<th>Max.</th>
<th>Min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.3</td>
<td>14.8</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>14.9</td>
<td>1.4</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
<td>11.3</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>4.7</td>
<td>8.2</td>
<td>1.4</td>
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<td>5.3</td>
<td>8.1</td>
<td>1.4</td>
</tr>
<tr>
<td>6</td>
<td>4.1</td>
<td>8.0</td>
<td>1.4</td>
</tr>
<tr>
<td>7</td>
<td>4.8</td>
<td>13.2</td>
<td>1.4</td>
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<td>8.3</td>
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<td>4.3</td>
<td>16.1</td>
<td>1.4</td>
</tr>
<tr>
<td>10</td>
<td>4.0</td>
<td>10.9</td>
<td>1.4</td>
</tr>
<tr>
<td>11</td>
<td>4.9</td>
<td>11.9</td>
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<tr>
<td>15</td>
<td>2.3</td>
<td>2.9</td>
<td>1.5</td>
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</table>

there needs to be diffusion and coalescence of these vacancies. Because of strain dependent migration [44] this is made easier when the initial structure is comprised of in–plane divacancies, than when there is a single vacancy. At the end of these cascades there is a higher possibility of divacancies and so will making it more likely for these extended defects will be nucleated.

A part of the reason simulations are run is to corroborate what is happening experimentally. Montet performed electron bombardment experiments [111, 112, 124]. A count of the number of vacancies was used as the measure of damage sustained by the graphite samples (as shown by the graph reproduced from the paper in Figure 4.26). This shows the count of single and of interlayer divacancies. This work involved a short anneal at 600 C in order to develop vacancies into etch pits which could be recorded, so for comparison with this work the simulations were done at the approximately that temperature
Figure 4.25: Plot showing the distance between a vacancy and its nearest vacancy. (a) average distance with the STDEV range and (b) shows the distances to all other vacancies. In both plots show the red trend line for the average distance \( y(x) = (-0.28 x) + 6.561 \).

\(~ 900 \) K. With the same lower PKA energies to match them in the plot. The results were similar with the single vacancies appearing at the same energy and the interlayer divacancy appearing at twice the energy of the single vacancy. This matches what was seen by Montet. For a more detailed analysis see reference [99].
Number of Defects

The count of the number of defects created in the cascade simulations, is done using the same code as before. The higher energy PKA’s can also produce a value for the TDE using the equation (4.2) by calculating the gradient of a graph of the number of defects versus the PKA energy.

As shown previously the cascades are directionally dependent, looking closely at two directions. The two plots in Figure 4.27 are the results from the simulations in the large graphite cell of $\sim 130000$ atoms at increasing PKA energies for these two directions. The first direction is $1\,1\,3$ which means it travels more in the prismatic direction. The other direction is $3\,3\,1$ that is travelling more in the basal direction. The number of defects formed at each energy are plotted in Figure 4.27(a) where the trends are set to go through the origin $y(x) = 10.6x$ for $1\,1\,3$ and $y(x) = 12.2x$ for $3\,3\,1$ and have a standard error of 2.2 and 2.8, respectively. Using the modified Kinchin–Pease equation (4.2) these trends produce a threshold displacement energy of 37.7 eV in the $1\,1\,3$ direction. Then when looking at the trend for $3\,3\,1$ direction in the plot it produces a lower displacement energy of 32.9 eV. The reason that the $1\,1\,3$ direction has a higher TDE is due to channelling as mentioned by Christie et al. [27] meaning fewer atoms are displaced at the beginning of the simulation. With fewer displacements the probability of defect formation goes down
Figure 4.27: Both plots are from the cascades in the two directions θ = 25°, φ = 45° (1 1 3) and θ = 76°, φ = 45° (3 3 1). Where (a) is the number of defects formed in the same large graphite cell with an increase in the displacement energy. With the calculated threshold displacement energy worked out from the gradient of the trend lines produced. Then (b) is the energy difference from the equilibrated graphite to the end structure after simulation from each different displacement energy.

leading to a higher TDE.

The energy for the final structure from all these simulations is compared with the equilibrated graphite cells total energy. This difference for each PKA energy can be seen in the plot in Figure 4.27(b) for both directions discussed. This plot produces a linear trend for both directions again going through the origin $y(x) = 120x$ for 1 1 3 and $y(x) = 128x$ for 3 3 1 and have a standard error of 25 and 27, respectively.
This difference in energy is a first estimate of stored energy, and is only approximate because defects can annihilate on longer timescales than are simulated here. Later on in this Chapter (4.4) the formation energy of each of these defects is calculated using EDIP. These can be used to compare the energy arrived at by defect counting (multiplying the formation energy of each defect by the number of those defects) with the energy calculated directly. Looking at just one PKA direction in this case 1 1 3 the only variable is the PKA energy which ranges from 25 eV to 1000 eV. The difference in energy from the end of the cascade simulations compared to the equilibrated graphite is seen in column two in Table 4.6. The third column is the energy for the types of defects seen summing over the count of each defect times their formation energy. For example at the PKA energy of 25 eV there are no defects so the energy would be 0 eV. Then at 50 eV PKA energy there is a single flat vacancy and a spiro interstitial which are separated by a single layer of graphene. The energy for these defects was added together and produced a value of 12.18 eV, which is close to the energy difference from the simulation energy.

<table>
<thead>
<tr>
<th>PKA</th>
<th>Difference</th>
<th>Defect</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>50</td>
<td>12.29</td>
<td>12.18</td>
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<tr>
<td>100</td>
<td>14.97</td>
<td>15.94</td>
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<td>250</td>
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<td>34.43</td>
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<tr>
<td>500</td>
<td>55.72</td>
<td>46.32</td>
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<tr>
<td>750</td>
<td>73.96</td>
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</tr>
<tr>
<td>1000</td>
<td>117.85</td>
<td>117.83</td>
</tr>
</tbody>
</table>

Table 4.6: The energy difference from the starting structure to the final structure from the simulations in the direction 1 1 3. The damage energy of the type of defects seen at the end of the cascade, at the different PKA energies.

The breakdown on the type of damage seen at the end of the simulations for each of the different PKA energies is shown in Table 4.7, where at each PKA energy the number of each type of defect seen is written. When all the defect energies are added up the match to the difference in total energies of the systems is very close. So this could be used as another way to identify the type as well as the amount of damage produced in the simulations. One interesting point to note is the direct production of both divacancies
Table 4.7: Defect types created in high energy cascades, at each PKA energy the type of damage created at the end of the cascade simulation of PKA direction 1 1 3 with the number of each.

<table>
<thead>
<tr>
<th>E (eV)</th>
<th>Link</th>
<th>Spiro</th>
<th>Grafted</th>
<th>Split</th>
<th>I2 bridge</th>
<th>Flat V</th>
<th>Hackelite</th>
<th>V2nn</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>250</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>500</td>
<td>1</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>750</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1000</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>0</td>
<td>1</td>
<td>7</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

and di-interstitials. Although they are relatively rare defects they could have impact on nucleation of vacancy lines and interstitial loops, which are normally regarded as needing diffusion to form.

Now we turn to temperature dependence in the cascade, comparing the cascade simulations at different temperatures of 300 K to 900 K averaged over a variety of directions. There are two plots in Figure 4.28, that are from the same simulations the only difference is that the first one Figure 4.28(a) is the number of defects, which is Frenkel pairs and Dienes defect (not counting the link defect). The second plot in Figure 4.28(b) is just the number of Frenkel pairs. Looking at the first plot of all defects produced ignoring the link defect, this produces a value of $E_{dd} = 32.4$ eV at 300 K and $23.3$ eV at 900 K. If the Dienes defect is ignored in the count then the TDE value increases, with $E_{dd} = 36.0$ eV at 300 K and $25.4$ eV at 900 K. The huge spread in gradients has two causes: first the inaccuracy of the fits which have large standard error ($2.5$ eV and $3.8$ eV for defects and $2.8$ eV and $3.5$ eV for just FP) and second from the question of whether to include D defects or not. There is a case to include D defects because they appear to arise from atomic displacement. The interesting question is whether they would etch similarly to a vacancy in Montet’s method [124]. There is some evidence that radiation at the higher temperature leads to lower damage.
Figure 4.28: Both plots are from the end of cascades averaged over different directions at 300 K (blue) and 900 K (red). Where (a) is the number of defects (FP and D), where 300 K trend is $y(x) = 0.01233x$ and 900 K trend is $y(x) = 0.01719x$. The second plot in (b) is just the number of FP, where 300 K trend is $y(x) = 0.01112x$ and 900 K trend is $y(x) = 0.01577x$.

Threshold displacement energy (TDE)

This section is still cascade simulations in graphite but now at a lower PKA energy, to calculate the threshold displacement energy. The theory behind this and the calculations can be seen in more detail in my paper [99]. The main difference between the results seen in the paper and here are that the simulations were done in 25 different direction but were only done in 22 directions for the paper. The graphite lattice has a point group symmetry.
of \( D3h \), which has the symmetry elements \( E \ 2C3 \ 3C2 \ \sigma h \ 2S3 \) and \( 3\sigma v \). To determine the distribution of PKA directions over the full range of solid angles, the corresponding symmetry operations were performed on the list of unit vector directions simulated. The resultant distribution of points are plotted on the surface of a unit sphere in Figure 4.29.

\[ \text{Figure 4.29: The blue points on the sphere represent all the directions simulated to calculate the threshold displacement energy taking into account the symmetry operations of the graphite lattice.} \]

These simulations where done using the two types of PKA: the first is an atom from an \( \alpha \) site the other is an atom from a \( \beta \) site. Starting at a PKA energy of 20 eV, where no defect is formed in any of the directions simulated. It is only when the PKA energy goes up to 25 eV is a defect (Frenkel pair and Dienes defect) formed without collapsing back down. When the energy gets up to 60 eV all the directions form a defect. The average number of defects over all directions is plotted against the PKA energy in the plot in Figure 4.30. There is not a significant difference between a PKA from an \( \alpha \) site compared with the PKA from a \( \beta \) site. Only that at the lower energies is it producing a defect in more directions from the \( \alpha \) site compared to the \( \beta \) site but this is most likely due to the choice of PKA directions which include the bond direction for the case of the \( \alpha \) atom, but not for the \( \beta \) atom.

Also plotted on this graph is the expected idealised trend according to the Kinchin–Pease model expressed in equation (4.1) with the displacement efficiency \( \kappa = 0.8 \) and \( E_d = 25 \) eV. The points at this low energy do not really follow this trend, being closer to a square root function. So a new plot with the same data is shown in Figure 4.31. This plot is showing a new function with the points at each PKA energy averaged over the \( \alpha \) and \( \beta \) site simulations. Here the new trend for the damage produced is \( N_d = \sqrt{\frac{E}{E_d}} \sqrt{E - E_d} \), which hits the linear trend at \( 2E_d \) which in this case is 50 eV.
Figure 4.30: Plot of the average number of defects created from an $\beta$ (blue) and $\alpha$ (red) site. Data from the small graphite cell is represented by squares and from the larger cell is represented with triangles. The Kinchin-Pease model is the black line.

Figure 4.31: Plot showing the average number of defects (FP and D) created at different PKA energies with a trend in red of $y(x) = a\sqrt{x - E_d}$ where $a = 0.16$ and $E_d = 25$ eV.

It is clear that the threshold region above the threshold (approximately 25-50 eV) the trend is square root of excess kinetic energy and the damage caused by the PKA alone, but in a cascade (made up of secondary displacement groups) there are SKA’s and TKA’s. As seen in the higher energy simulations the trend for the number of defects formed at different PKA energies is linear. Trying to reconcile these two trends gives rise to a new damage function.
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Damage function

This new damage function was first mentioned in my TDE paper [99], so this section will be an overview.

From these lower energy cascades a new damage function can be seen where there is a square root trend that starts at the threshold energy ($E_d$). The trend will then change into a linear trend at twice the threshold energy ($2E_d$). Which can be expressed as:

$$N_d = \begin{cases} 
0 & 0 < E < E_d \\
\kappa \frac{E}{E_d} \sqrt{E - E_d} & E_d < E < 2E_d \\
\kappa \frac{E}{2E_d} & 2E_d < E 
\end{cases}$$

(4.3)

which is plotted in Figure 4.32, when $E_d = 25$ eV and $\kappa = 0.8$. Equation (4.3) is made simpler if we take $\epsilon = \frac{E}{E_d}$, and the function can now be expressed as equation (4.4).

$$N_d = \begin{cases} 
0 & 0 < \epsilon < 1 \\
\kappa \sqrt{\epsilon - 1} & 1 < \epsilon < 2 \\
\frac{\kappa \epsilon}{2} & 2 < \epsilon 
\end{cases}$$

(4.4)

If the SKA, TKA, etc. act in the same way as the PKA then the total damage will be a sum of the functions for each. If we take the function for each knock-on atom $f_m(\epsilon)$, expressed in equation (4.5) and combine them together to get the total amount of damage
(equation (4.6)).

\[
\begin{align*}
    f_m(\epsilon) = \begin{cases} 
    0 & 0 < \epsilon < m \\
    \kappa_m \sqrt{\epsilon - m} & m < \epsilon 
    \end{cases} 
\end{align*}
\]  

(4.5)

\[
N_d = f_1(\epsilon)(1 + f_2(\epsilon))(1 + f_3(\epsilon)) 
\]  

(4.6)

This would be the function if all knock-on atoms act the same.

Cascade simulations were then performed where the PKA is an interstitial atom, which is the case for the SKA and TKA. These simulations were done the same way as when a PKA is chosen from a lattice site, the only difference is the simulations could only be done at 0 K because otherwise the thermal motion of the interstitial atom created problems. The average number of defects are plotted in the Figure 4.33. It is clear from this that

![Figure 4.33: Taking from TDE paper [99], showing the number of defects produced when the PKA is an interstitial atom. The red trend line is \(y(x) = 0.04811\sqrt{x} - 55\).](image)

the PKA and the SKA will not act in the same way. As the plot shows that the threshold is around two times that from the PKA simulations. This will change the function for the other knock-on atoms, shown in equation (4.7).

\[
\begin{align*}
    f_m(\epsilon) = \begin{cases} 
    0 & 0 < \epsilon < 2m - 1 \\
    \kappa_m \sqrt{\epsilon - (2m - 1)} & 2m - 1 < \epsilon 
    \end{cases} 
\end{align*}
\]  

(4.7)

\[
N_d = f_1(\epsilon)(1 + f_2(\epsilon))(1 + f_3(\epsilon)) 
\]  

(4.8)

Using this new function we get a plot that looks like Figure 4.34 with the data from the plot in Figure 4.31. The trend lines are from equation (4.8) where \(\kappa_1 = 0.73\), \(\kappa_2 = 0.19\) and
The cascade simulations were also performed in other carbon structures, i.e. diamond and amorphous carbon structures. These are the same starting structures that were used in the thermal spike simulations, (provided by N. Marks) previously mentioned. These simulations are not as extensive as in graphite as they are used to get an insight into the qualitative differences between graphite and these other materials. The amorphous structures have densities 1.5 g/cc (glassy carbon) and 2.0 and 3.0 g/cc (tetrahedral amorphous ta-C).

An example of the path of the PKA (direction 1 1 2) in the cascade in each of these different structures can be seen in the examples of Figure 4.35. In the Figure 4.35(a) you can see the distance the PKA has travelled in the diamond structure is not very far compared to graphite, even with an energy of 1 keV. The PKA has travelled further in the amorphous structure which has a lower density than the diamond. Unlike the structure of graphite there can be no channelling in the higher density amorphous structures.

The distances the PKA travelled through these four carbon structures is compared to the graphite simulations. This is done by investigating all the distance the PKA travels in the carbon structures in the fifteen different directions (111, 112, 113, 114, 131, 133, 141,
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Figure 4.35: Cascades at 300 K with a PKA energy of 1 keV in the direction 1 1 2 with respect to the axes of the cubic cells used. The path of the PKA is highlighted in red, with the image being the final structure at the end of the simulations. The structures are (a) diamond and amorphous carbon with a density (b) 1.5 g/cc, (c) 2.0 g/cc and (d) 3.0 g/cc.

144, 215, 311, 313, 331, 411, 414 and 441) with energies ranging from 250 eV to 1000 eV. The plots for the average distance travelled in diamond is in Figure 4.36. The diamond structure stops the PKA the quickest of the structures looked at in this study. This is not surprising as diamond has the highest number density of atoms of all solids. When compared to the plots for amorphous carbon at different densities shown in Figure 4.37, these show that the PKA can travel the furthest in the glassy carbon structure as you
can observe the PKA find a path with very little obstruction. The ta–C with different densities stops the PKA quicker at 3.0 g/cc than at 2.0 g/cc, which is expected. The other two amorphous carbon structures stop the PKA from travelling as far as it would in graphite. Even with a lower density of 2.0 g/cc, this is due to there not being the space between the layers which are seen in the graphite structure.

In diamond when the PKA is given energy it collides with a carbon atom which then bumps into its neighbour creating an atomic displacement wave that travels through the structure. This wave goes to the edges of the cell where it is damped by the thermostat. The wave is not seen in the graphite simulations. Due to diamond’s radiation hardness [125] not many defects are formed. The only defect really seen in these simulations is the bond swap defect, just like in the thermal spike (Figure 4.11). The damage done to the diamond structure can be seen in the example Figure 4.38 with different PKA energies. Even at the higher energy PKA of 1 keV very little damage is seen at the end of the simulation (Figure 4.38(d)).

Looking at all the simulations at 300 K and counting all the defects at the end of the cascade after quenching, the average number of defects is plotted in Figure 4.39, with the STDEV range. Compared to graphite very few defects are seen at the end of the cascades. This plot indicates a threshold displacement for diamond of $E_d = 77.7$ eV from the KP model and displacement efficiency $\kappa = 0.8$. Another important observation that this plot shows is that displacement damage in diamond is not directionally dependent as would be
Figure 4.37: Plots of the average distance travelled by the PKA in amorphous carbon with a density of (a) 1.5 g/cc, (b) 2.0 g/cc and (c) 3.0 g/cc. The blue squares are the average distance and the blue lines are the STDEV range. The dotted trend line is from the graphite cascade simulations and the red lines are the trend lines from the data (a) $y(x) = 0.006775x$ (b) $y(x) = 0.004456x$ (c) $y(x) = 0.002906x$. 
Figure 4.38: Quenched diamond structure after cascades of different energies. The simulations were done at 300 K in the direction $1\ 1\ 2$ with a PKA energy (a) 250 eV, (b) 500 eV, (c) 750 eV and (d) 1000 eV. The blue sphere represents a missing atom from the structure and the red is an extra (interstitial) atom.

expected from its cubic symmetry. This also means there is a small range in the number of defects seen at each of the PKA energies.

4.3.3 Discussion

In the cascade simulations just as with the thermal spike simulations, energy is added to the system at the beginning and the results come from how the graphite reacts. Though there is less energy added to the graphite than with the thermal spikes, more damage is observed at the end.

The damage that is observed after the graphite has been quenched are mainly the
Figure 4.39: Average number of defects at the end of cascades in diamond at 300 K. Showing the small STDEV range and the red trend line $y(x) = 0.005147x$. Compared to graphite with the black dashed trend line.

Frenkel pairs (made of vacancies and interstitial atoms). One observation is that the damage placement is dependent on the direction the PKA. All the cascades match the image from Thrower [21] (Figure 1.4) with the PKA having branches coming out of the PKA’s path creating displacement groups.

The majority of the damage occurs at the end of the simulations, i.e. at the end of range for the cascade, where the number of knocked on atoms is the greatest. We also see divacancies at the end of the cascade group, which will mean that larger groups of defects can form due to the migration of other single vacancies within the strain fields of divacancies as mentioned by Trevethan et al. [44].

The number of defects produced in these simulations was used to calculate the threshold displacement energy. There is some ambiguity on which defects are being detected in many of the reports of the damage threshold. In the case of Montet [124] the vacancies were counted directly and the results are shown in the plot shown in Figure 4.26. The count in this study is presented either as just from the number of Frenkel pairs or the number of Frenkel pairs and Dienes defect (collectively called defects). Looking at the extra potential energy in the system due to the defects in the graphite is a measure of stored energy but it can also be used as a confirmation of the number and type of damage produced.

The higher energy (linear trend) data produces a TDE value $E_d \sim 25$ eV but with significant uncertainties. With the threshold simulations at the lower energy 25 eV is the
energy that a defect is first created and stable.

The results for these lower energy PKA’s match the theory of the Kinchin–Pease model in so far as \( N_d > 0 \) at \( E_d \) and when the PKA reaches \( 2E_d \) then more than one defect is created. Between \( E_d \) and \( 2E_d \) a new function is seen of \( N_d = \frac{c}{\sqrt{E_d}} \sqrt{E - E_d} \) at \( E_d < E < 2E_d \). Also seen is how the PKA is more likely to create defects compared to the SKA, and the SKA will likewise create more compared to the TKA and so on.

The cascade simulations have highlighted how different graphite acts compared to other materials just like the thermal spike did. As diamond is more dense the PKA can not travel as far and the paths look very different. Only a small amount of damage was produced in the diamond cascades but when formed at the beginning of the cascade it did not heal like the damage in the graphite cascades. For the amorphous carbon the displaced atoms are harder to track but the distance of the PKA is clear. With the lower density of the material the PKA can travel further, which is to be expected.

### 4.4 Point defect energy validation EDIP vs DFT

N. Marks posed the question of the validity of EDIP in displacement damage calculations, which this chapter attempts to answer. For a comparison of EDIP and ZBL potential with DFT (in this case the AIMPRO program) the formation energy of point defects were compared. A more in depth comparison that includes the adaptive intermolecular reactive bond order (AIREBO) [65] can be seen in one of my papers [126].

#### 4.4.1 Method

The structures for the defects were previously created by C. Latham, and his results from LDA and GGA calculations are used for a comparison [126].

To find the formation energy of the defects using EDIP the steepest descent algorithm is used to find the minimum or stable point. This is done by setting the velocities to zero, and running until the temperature reaches 0 K. An example of what is happening during these simulations can be seen in Figure 4.40. This shows the energy lowering until it flattens out. This is a nearby energy minimum from the starting structure. It is not important that the energy minimum is a global one, but just one that is close to the one obtained using DFT which gave the starting structure. Each simulation varies in length as the time depends on how quickly the temperature of the system goes to absolute zero.
The formation energy ($E_f$) is calculated using equation (4.9)

$$E_f = E_H - (N_H \frac{E_p}{N_p})$$

(4.9)

where the total energy of the graphite structure with the defect ($E_H$) is compared with the total energy of perfect $AB$ stacked graphite ($E_p$). $N_H$ is the number of atoms in the defect structure, $N_p$ is the number of atoms in the $AB$ stacked graphite reference cell.

### 4.4.2 Results

The formation energies for different types of interstitials can be seen in Table 4.8. This shows all the interstitial structures and the energies calculated using EDIP and the DFT results from C. Latham. A clear way to see the comparison is with the plot in Figure 4.41 where the LDA results are plotted against the EDIP results.

The EDIP values for the $\alpha$ and the $\beta$ split–interstitial have the same value, due to there not being an interaction between the layers with EDIP. So only with DFT does the $\alpha$ and the $\beta$ position show a difference in the formation energy. The single interlayer interstitial which is also known as the spiro–interstitial [36] comes to the same value seen in DFT–LDA but structurally looks different (Figure 4.42). EDIP penalizes small rings of C (e.g. the triangles seen in the spiro–interstitial), so the lowest energy structure is singly bonded to graphitic layers. The majority of the interstitial values are higher with EDIP compared to the DFT calculations.
Then looking at the vacancies and the Dienes defect, the formation energies for these structures are in Table 4.9. These results are again plotted, just like the interstitial results, in Figure 4.43. This shows clearly that the vacancies have a lower value with EDIP in comparison with DFT, with the green trend line showing the 1 : 1 ratio, and the red trend from the data points giving \( E_{(EDIP)} = 0.91E_{(DFT-LDA)} - 0.97 \) eV.

The formation energies calculated using EDIP have been compared with the DFT–LDA and DFT–GGA values and show a reasonable agreement within \( \sim 30\% \).

The EDIP simulations also produce a defect that is not stable in DFT calculations: this is the link defect which has previously been mentioned. This defect is when two

<table>
<thead>
<tr>
<th>Defect Structure</th>
<th>Formation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDIP</td>
</tr>
<tr>
<td>Single interlayer interstitial</td>
<td>5.85</td>
</tr>
<tr>
<td>( \alpha ) split–interstitial</td>
<td>9.61</td>
</tr>
<tr>
<td>( \beta ) split–interstitial</td>
<td>9.61</td>
</tr>
<tr>
<td>Grafted interstitial</td>
<td>7.85</td>
</tr>
<tr>
<td>Bipentagon grafted interlayer bridge</td>
<td>10.96</td>
</tr>
<tr>
<td>( \alpha-\beta ) double interlayer bridge</td>
<td>9.59</td>
</tr>
<tr>
<td>( \beta-\beta ) bent interlayer bridge</td>
<td>9.03</td>
</tr>
<tr>
<td>Bipentagon interlayer bridge</td>
<td>6.79</td>
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<tr>
<td>Twin–triangle interlayer bridge</td>
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</tr>
<tr>
<td>Flat twin–triangle interlayer bridge</td>
<td>10.02</td>
</tr>
<tr>
<td>( \alpha-\beta ) bent interlayer bridge</td>
<td>8.89</td>
</tr>
<tr>
<td>Twisted twin–triangle interlayer bridge</td>
<td>9.04</td>
</tr>
<tr>
<td>( \alpha-\alpha ) arch bridge</td>
<td>9.25</td>
</tr>
<tr>
<td>( \beta-\beta ) arch bridge</td>
<td>9.31</td>
</tr>
<tr>
<td>Skew bipentagon interlayer bridge</td>
<td>8.21</td>
</tr>
<tr>
<td>( \alpha-\beta ) double split pair</td>
<td>12.82</td>
</tr>
<tr>
<td>Isolated pentagon interlayer defect</td>
<td>13.72</td>
</tr>
</tbody>
</table>

Table 4.8: Formation energies of interstitials using EDIP compared to DFT with LDA and GGA calculations. The structure labels are as given in Latham et al. [36].
Figure 4.41: The formation energy of the interstitials calculated in EDIP and DFT-LDA comparison. The green line shows a 1:1 ratio going through the origin, the red line is the trend $y(x) = 0.822x + 2.258$, showing the EDIP values are high in EDIP compared to DFT.

![Graph](image)

Figure 4.42: Single interlayer (spiro) interstitial after DFT calculation (a) and after EDIP calculation (b). The EDIP structure has only one bond to each layer because 3 atom rings are higher in energy than they should be.

![Images](image)

(a) ![Images](image) (b)

Atoms in layers next to each other are pinched close together and link. This can be seen in Figure 4.44 highlighted by the red atoms. The reason that the atoms link is an artificial local minimum in energy coming from the EDIP functional form. Forming an $sp^3$ carbon reduced the strength of its bonds to its three neighbours, and presumably this penalty in EDIP is not large enough compared with the energy reduction in forming the interlayer bond. This defect has an apparent EDIP formation energy of 1.88 eV.
CHAPTER 4. MD SIMULATION OF IRRADIATION DAMAGE OF GRAPHITE

<table>
<thead>
<tr>
<th>Defect Structure</th>
<th>Formation Energy (eV)</th>
</tr>
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<tr>
<td>Flat, reconstructed α vacancy</td>
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</tr>
<tr>
<td>Flat, reconstructed β vacancy</td>
<td>6.33</td>
</tr>
<tr>
<td>Haekelite structure divacancy</td>
<td>6.32</td>
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<td>Close α–β divacancy</td>
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<td>Offset trans 3rd neighbour divacancy</td>
<td>12.50</td>
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<tr>
<td>Cis 3rd neighbour divacancy</td>
<td>13.23</td>
</tr>
<tr>
<td>C2 single cross BB close divacancy</td>
<td>12.66</td>
</tr>
<tr>
<td>C2h cross β–β next divacancy</td>
<td>13.44</td>
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<tr>
<td>Cs cross α–β divacancy</td>
<td>13.44</td>
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<td>C2h double–cross BB close divacancy</td>
<td>13.01</td>
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<tr>
<td>Dienes defect</td>
<td>5.58</td>
</tr>
</tbody>
</table>

Table 4.9: Formation energies of vacancies using EDIP compared to DFT with LDA and GGA calculations. The structure labels are as given in Latham et al. [127].

Figure 4.43: The formation energy of the vacancy calculated in EDIP and DFT-LDA comparison. The green line shows a 1:1 ratio going through the origin, the red shows the trend $y(x) = 0.91x - 0.97$. 
4.5 Discussion

One of the clear observations is how resilient graphite is as shown in the thermal spike simulations when very little damage is created even in the higher ranges of energy that can be achieved by the initial PKA. With the high amount of energy going into each layer, graphite shows a high resilience to amorphisation. This means that in graphite very little damage is produced by the PKA when it travels through the graphite before collisions occur. The defects that are formed are mainly intimate Frenkel pairs at the higher energies. These intimate Frenkel pairs are likely to collapse in the higher temperature ranges seen in nuclear reactors.

Diamond damages less (due to the high Frenkel pair energy of $>20 \text{ eV}$ [128]) and has a quicker recovery than graphite probably from a combination of higher defect mobility and thermal conductivity. Also with the diamond you can see the energy disperse more clearly than in the layered structure of graphite. The thermal spike simulations in defective graphite help the migration of the defects at the high energies of a thermal spikes. This means that the thermal spikes have the potential to heal damaged graphite.

During the cascades graphite is unique, as it does not behave in any way like the other carbon structures simulated. In diamond a shock wave travels through the structure but with graphite the PKA passes through the layers causing very few defects to be formed. The defects formed are the same as the structures seen in DFT studies.

More damage is at the end of the cascade simulations than in the thermal spikes even though a cascade has less energy going into the system. The majority of damage is at the end of the PKA’s path through the graphite. A threshold displacement energy of 25 eV is calculated using two methods. The first is the high energy cascades using the adapted Kinchin and Pease method. The second is with the lower energy near threshold PKA
simulations that showed a 25 eV threshold and a near square root trend.

A new damage function was created to take into account the damage produced by the different knock-on atoms. It was shown that the PKA is more efficient at creating damage than the SKA and this is thought to be due to retrapping of the SKA by the vacancy created when it displaces another atom.

The formation energy values for interstitials using EDIP are higher than the DFT calculated values but the energies for the vacancies are lower. Considering that EDIP was created for simulation of amorphous carbon the values achieved with energy minimisation producing values comparable to DFT calculations is encouraging.
Chapter 5

Polycrystalline graphite

In the nuclear reactors the graphite moderator is polycrystalline, and this means that it is made from $AB$ stacked crystalline regions which are all misoriented with respect to each other. So this section will look at cascades within or through the grain boundary.

5.1 Introduction

Simulations and calculations of single crystal graphite and graphene can be found in abundance in the literature but there are only a few that have been performed with polycrystalline graphene; one recent study looks at the thermal conductivity of these polycrystalline graphene sheets [129]. Also Delannay et al. model cracking within and between the grains using Finite Element Methods [130]. Both of these are 2D models, so there is a large gap in the theory for 3D models of polycrystalline graphite.

There is more literature on experiments using polycrystalline graphite, because this is the real material in use in industry. In Chapter 4.3 there is Table 4.4 showing the TDE results in literature. The first result in the table is an experiment by Eggen. This was electron irradiation of polycrystalline graphite and produce a result of $24.7 \pm 0.9$ eV (referenced by Thrower [34]). Also mentioned before in Chapter 1.4 there is the dimensional change. There have been many experiments that study polycrystalline graphite under neutron irradiation to observe the dimensional and structural change [131, 132, 133].

In this chapter, two different models of polycrystalline graphite and grain boundaries are employed to investigate the behaviour of cascades in non-crystalline regions of the bulk material. In the first model, the facets of tesselating crystallites define their termination,
CHAPTER 5. POLYCRYSTALLINE GRAPHITE

which results in an over-coordinated high density boundary. In the second model, atoms
are removed near the crystallite facets to produce a grain boundary with lower density and
coordination. Both these polycrystalline models were constructed (by T. Trevethan [134])
using the fillatoms code [135] which uses the Qhull program for the construction of the
Voronoi diagram [136].

5.2 Structure I

5.2.1 Method

The polycrystalline graphite structures are created in a simulation cell with periodic
boundary conditions imposed in all three dimensions. The crystallites are defined by
a Voronoi tesselation of polyhedra, with random nucleation sites, and in this system there
are 5 crystallites. Once the polyhedra is defined within the simulation cell, they can be
filled with atoms positioned according to the lattice structure of the crystal with random
lattice orientations. Initially, the facets of the polyhedra then simply define the termina-
tion of the crystallites surface, which will be completely randomly oriented. The grain
boundaries formed in this construction have a tendency to be composed of a high propor-
tion of over coordinated (sp3) atoms, and the total density of the system is 99.6 % of that
of the single crystal [134]. An example structure can be seen in Figure 5.1 where the red
lines highlight the border around the sections (grain boundaries).

Figure 5.1: A cross section of the polycrystalline graphite structure, clearly showing the grain boundaries between
the sections of $AB$ stacked graphite.
The simulations in this section are performed in the same way as the graphite structure in the previous chapter. The simulations are done using the EDIP and ZBL potential. The system will be equilibrated at different temperatures from 0 K to 1200 K and from these the cascade simulations are set off. These simulations will be with a PKA of different energies and different directions just like the single crystal graphite simulations.

The system has fixed atoms and a thermostat just like the structures from the previous chapter. The simulated cell structure is shown in Figure 5.2. In this case the red atoms show the fixed atoms and the blue are the thermostat. The thermostat and fixed atoms go completely around the cube but in the Figure 5.2 this is not shown to produce a clear diagram of the structure and the thickness of these regions. The number of atoms in the system is $\sim 120000$.

### 5.2.2 Results

In Figure 5.3 with the disorder at the grain boundaries, it is hard to see what is happening. A way to see these grain boundaries is to focus on the coordination of each atom in the system. This is done using a custom code that was written by T. Trevethan, which defines the coordination of each atom [134]. From the initial structure we can see the coordination of 1 to 4 from the coloured atoms seen in Figure 5.3. The grain boundaries can be clearly seen with the disorder from the red and green atoms representing a coordination of 2 and 4 respectively. There are a few blue in the structure which represents the coordination of 1. The grey lines represent the graphite honeycomb structure where atoms have a

![Figure 5.2: A cross section of the polycrystalline graphite structure, clearly showing the fixed atoms in red and the thermostat in blue.](image)
Figure 5.3: Polycrystalline graphite structure, equilibrated at 300 K. This shows the coordination of all the atoms. The colours represent the coordination as follows: 1 is blue, 2 is red, 3 is grey and 4 is green.

coordination of 3.

Equilibration

The structure seen in Figure 5.3 was equilibrated at different temperatures: 0 K, 300 K, 600 K, 900 K and 1200 K. The resulting structures are then compared to the original structure to see how many of the atoms change coordination. This can be seen in the plot in Figure 5.4, which shows as the temperature increases more atoms change coordination. This trend is what you would expect to see as with more temperature in the system there is the required energy for the atoms to break bonds.

Now instead of looking at just the number of atoms that change coordination we look instead at the number with a certain coordination. Looking at all the temperatures equilibrated in Table 5.1 gives the total number of atoms with each coordination of between 1 and 4 in the structure. It also shows the percentage of atoms with that coordination in the system. The table shows the initial coordination in the last row. For the comparison the percentage of atoms with a type of coordination is compared to the initial percentage of atoms with the same type of coordination.
CHAPTER 5. POLYCRYSTALLINE GRAPHITE

Figure 5.4: The number of atoms that change coordination at different equilibration temperatures shown with the blue points and produce a trend (red) \( y(x) = 976 \log(x) - 1015 \).

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<thead>
<tr>
<th>( T ) (K)</th>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>( % ) from all atoms</th>
<th>1</th>
<th>2</th>
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<td>107611</td>
<td>1075</td>
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<td>8053</td>
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<td>8.178</td>
<td>89.119</td>
<td>0.890</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1: The coordination of the atoms in the structure that range from 1 to 4 at different temperatures. The initial coordination before the simulations is at the bottom of the table.

This comparison is shown clearly in Figure 5.5 with the difference in the percentage of different coordinations against the temperatures. With the gain in temperature the clearest change is in the number of atoms with coordination of 3, which goes up. This is what was expected as the structure at the boundaries becoming more graphitised. After 300 K there is not much change in the coordination. Applying this temperature has made the structure more stable so very little change happens at the higher temperatures.

The most interesting points in this plot is the yellow point for the 4 coordination. On first raising the temperature the number goes down but when temperature is raised again the number of coordination 4 goes back up. It is possible that thermal expansion in the
constant volume simulations encourages the diamond structure at these high temperatures.

Cascade

The cascade simulations were performed using the structure equilibrated at 300 K as this structure is most like perfect graphite. These simulations will have a range of PKA energies, from 250 eV to 1000 eV. The PKA was set off in 15 different directions (same as before Chapter 4.3.2) in each case.

A comparison of the cascade simulation through perfect AB stacked graphite and the polycrystalline graphite can be seen in Figure 5.6. This shows the PKA travelling through the layers in Figure 5.6(a) the same simulation is then performed in the polycrystalline structure in Figure 5.6(a). From the graphite MD simulations it was shown that the results were dependent on the PKA direction.

When the PKA travels through a grain boundary then the direction will be changed. So when the PKA is set off in the same direction as with the graphite the direction of travel will depend on the orientation of the crystal it is travelling in and also the change when it goes through a grain boundary. This can be seen when zoomed into the path from Figure 5.6(a) (Figure 5.7). When the PKA path moves (represented by the red line) from one crystal to the next you can see a bend in the path. This means that it is directionally dependent in each crystal and the major factor will be how it acts between each crystal.
Figure 5.6: Diagrams showing a comparison of cascades in perfect and polycrystalline graphite: (a) perfect graphite structure and (b) is polycrystalline graphite. The direction of the PKA is $\theta = 45^\circ$, $\phi = 55^\circ$ for both with a PKA energy of 1 keV. Figure (b) is cut so that you can see the path clearly.

(Cascade distance)

The direction of the PKA changes in the polycrystalline structure, so the distance travelled by the PKA could also be affected. Cascade simulations were performed at 300 K in 15 different directions for each PKA energy. These can be seen in Table 5.2 with the average distance the PKA travels in the simulations with the standard deviation (STDEV). The simulations with a PKA of 750 eV has the largest spread of PKA travelling distances. When these distances are compared to single crystal graphite, the trend on the plot in

<table>
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<th>Energy (eV)</th>
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<th>STDEV (nm)</th>
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<td>1.46</td>
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Table 5.2: The PKA's average distance travelled in simulations at 300 K at different PKA energies. With the range for each of the PKA energies.
CHAPTER 5. POLYCRYSTALLINE GRAPHITE

Figure 5.7: Section of the polycrystalline graphite cascade with PKA energy 1 keV in the direction of $\theta = 45^\circ$, $\phi = 55^\circ$. The structure is rotated to highlight the change in crystal orientation and the path is shown in red.

Figure 5.8, seems to be lower. The grain boundaries seem to have an effect. The PKA does not travel as far in the polycrystalline structure at the higher energy PKA cascades but at the lower PKA energy of 250 eV the point lies on the trend for graphite. This could be due to the fact the PKA does not interact with a grain boundary in these simulations. So only at the higher PKA energies does the atom reach the different grain boundaries.
and is slowed down faster than in a single crystal.

**Cascade damage**

The damage is harder to track in these simulations, compared to the cascades previously done in a single crystal. Cascades performed at 300 K which are quenched down to 0 K. The damage is identified with the same custom code that was used to analyse the damage produced in the simulation in the single crystal graphite. This not only shows the damage created by the PKA but also the movement in the layers, which appear (Figure 5.9 as solid regions of interstitials (red atoms) over vacancies (blue atoms).

![Figure 5.9](image)

Figure 5.9: A quenched structure after a cascade with a PKA energy of 1 keV at 300 K in the direction of <1 1 1>. The blue atoms show a vacancy site and the red atoms represent an interstitial. Where they appear together in a given region, this depicts the movement of layers within the structure. The red line shows the path of the PKA which is shown in the zoomed in area.

This movement in the layers makes counting the number of defects more complex. So to track the damage the counting of the defects is focused on and around the path of the PKA. This means that it is mainly the damage produced from the PKA that is counted, which means that the damage from the SKA or the TKA are not included in the count of defects.

Looking at the highlighted section in Figure 5.9, the number of defects was counted from the blue atoms (vacancies) where there was not a red atom directly above the blue one. In each structure the count was only around the zoomed area.
<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Av. Damage</th>
<th>STDEV</th>
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<tr>
<td>1000</td>
<td>8.71</td>
<td>3.05</td>
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</table>

Table 5.3: The average damage (average number of vacancies) produced by the PKA in simulations at 300 K at different PKA energies. With the range for each of the PKA energies.

These results are plotted in Figure 5.10(a), with the standard deviation range. This shows less damage than seen in graphite, when comparing the linear trends. As with the plot for the distance travelled (Figure: 5.9) at the lower PKA energy of 250 eV the point is closer to the graphite trend. As the PKA energy rises and reach the higher energy of 1 keV, very little damage is seen in comparison with the single crystal graphite.

The graphite trend produces a trend for the $E_d = 27.0$ eV whereas the polycrystalline linear trend produces a value of $E_d = 42.0$ eV. This is lower due to the larger value for the gradient of the plot, which is due to the points form the higher energy PKA. With the damage being counted mainly caused from the PKA and not any SKA or TKA’s. The result from the 250 eV PKA energy being similar to the graphite single crystal could be due to the fact there is little to no damage done from any SKA but when the PKA energy increases more damage will be produced from SKA’s and at the higher range from the TKA’s.

In the TDE study shown in Section 4.3.2 there was a square root trend that was applied, for the PKA and the SKA. As these results are mainly from the PKA the square root trend was applied to the plot in Figure 5.10(b). This plot produces a very high threshold energy, and is not an accurate way for finding the damage just for the PKA as SKA damage could have been counted. A more reliable count of the total damage caused in this polycrystalline structure is needed.

**Cascades at absolute zero**

To be able to see all the damage produced in the cascade, the simulations were performed from the polycrystalline structures that were equilibrated at the high temperature of 1200 K. This structure is used as the change of coordination has tapered off, which can
CHAPTER 5. POLYCRYSTALLINE GRAPHITE

Figure 5.10: The average number of defects caused by the PKA in the cascade simulations at a range of PKA energies. The cascade simulation was performed at 300 K and then quenched to find the damage. The y-axis error bars show the STDEV of each point. In (a) the red line shows the linear trend of $y(x) = 0.009512x$ and the black dashed trend line comes from the high energy PKA damage in the single crystal graphite cascade at 300 K. In (b) the red line showing the trend of $y(x) = 0.3049\sqrt{x} - 161.5$ for the polycrystalline structure.

be seen in plot in Figure 5.4. The structure is then quenched down to 0 K, to stop further movement in the layers. The cascade simulations were then performed at a background temperature of 0 K, with the PKA set in the same directions and energies as those done at previously at 300 K.

The distance the PKA travels is not as far compared to the same simulations done at the higher temperature, which is what would be expected. The distances can be seen in
Table 5.4, with the ranges of the data shown. The range at 500 eV is the highest and

<table>
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<th>Energy (eV)</th>
<th>Av. Distance (nm)</th>
<th>STDEV (nm)</th>
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<td>1000</td>
<td>2.74</td>
<td>1.42</td>
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</table>

Table 5.4: The PKA’s average distance travelled in simulations at 0 K at different PKA energies. With the range for each of the PKA energies.

this is due to two simulations in the direction of 1 4 1 and 1 4 4. These two travel the furthest as they have found a channel in the structure, which means there is very little interactions between the PKA and the surrounding carbon atoms. This is highlighted in the plot from Figure 5.11, looking at the point when the PKA energy is 500 eV. Due to

Figure 5.11: The average distance travelled for a PKA in the cascade simulations at 0 K in polycrystalline graphite for different PKA energies. The y-axis error bars show the STDEV of each point, with the red line showing the linear trend of $y(x) = 0.003137x$ for the polycrystalline structure. The black dashed trend line is for comparison of the cascade simulations at 300 K.

the boundaries in the structure channelling is generally inhibited when compared to the single crystal graphite but overall the PKA will travel a smaller distance at 0 K compared with the 300 K simulations.

The damage is clearer to define in these simulations at 0 K compared to the earlier simulations. There are only a few movements that are not due to the cascade which can
be seen in Figure 5.12. There is no movement of the layers which was seen at 300 K

![Figure 5.12: Quenched structure after a cascade with a PKA energy of 1 keV at 0 K in the direction of 1 1 1. The blue atoms show a vacancy site and the red atoms represent an interstitial, they also show the movement of layers within the structure. The red line shows the path of the PKA which is shown in the zoomed in section.]

seen in Figure 5.9. Even though the simulations were set off in the same direction and with the same energy the path is different in the two diagrams.

The damage is now counted for the entire cascade simulation, by counting the number of vacancies. This means that at the higher energies there will be more damage seen in the results from the 300 K simulations. The count of damage is shown in Table 5.5. These results are plotted in Figure 5.13, with the standard deviation range, as before. This plot shows more damage being seen at the higher energies than in the previous results but at the lower PKA energy of 250 eV the damage is the same. With this plot there is a clear linear trend unlike the 300 K that had a square root trend. With this linear trend

<table>
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<th>Energy (eV)</th>
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<tr>
<td>1000</td>
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<td>5.97</td>
</tr>
</tbody>
</table>

Table 5.5: The average damage produced by the PKA in simulations at 0 K at different PKA energies. With the range for each of the PKA energies.
Figure 5.13: The average number of defects caused by the PKA in the cascade simulations at a range of PKA energies. The cascade simulation performed at 0 K and then quenched to find the damage. The y-axis error bars show the STDEV of each point, with the red line showing the linear trend of $y(x) = 0.01767x$ for the polycrystalline structure. The black dashed trend line comes from 300 K simulations.

there is a TDE of $E_d = 22.6$ eV. This is very similar to what is seen graphite, but it is a little smaller. This shows that the grain boundaries produce more damage in the cascade simulations.

In the simulations when the PKA ends at the grain boundary there is a cluster of displacements. The defects can become trapped in the grain boundary. This can be seen in Figure 5.14. Here it is shown clearly with the large number of blue atoms (vacancies) and red atoms (interstitials) at the end of the PKA’s path (trapped in the grain boundary).

Figure 5.14: Section of the polycrystalline structure after a cascade at 0 K. With a PKA energy of 1 keV in the direction 3 1 1. With the red line showing the path of the PKA, and the red and blue atoms highlighting the damage, especially that trapped in the grain boundary.
This has been seen in the tilt grain boundary in Martino et al. simulations [137].

5.3 Structure II

5.3.1 Method

In the second model of polycrystalline graphite, the simulation cell is constructed in the same way as before, however in this case the outermost layer of atoms is removed from the facets of each crystallite. This has the effect of reducing the density and the average coordination of atoms in the boundary regions.

The simulations are performed exactly the same way as the first structure was simulated. This means that the same temperature range was used (0 K to 1200 K) and the PKA energies and directions are also the same. Both structures have the same volume, though this new structure has fewer atoms of \(\sim 116000\) atoms. The number of atoms that are fixed is the same though and the thermostat is also the same.

5.3.2 Results

The structure can be seen in Figure 5.15, which shows the coordination of each atom. The same colour code applies to this structure. The most noticeable difference is the number of green atoms (coordination 4), which there are fewer of in this case. This can be seen more clearly in Figure 5.16, which shows a grain boundary from both structures side by side. The grain boundaries have healed differently under the equilibration of 300 K.

Equilibration

Just like the first structure this one is also equilibrated at different temperatures: 0 K, 300 K, 600 K, 900 K and 1200 K. When these structures are compared to the original structure to find the number of atoms that have changed coordination at these different temperatures. This is plotted in Figure 5.17, and just like the plot in Figure 5.4 the number of atoms that change coordination increases at the higher temperatures. The main difference between structure I and this structure is at the lower temperature of 300 K there are few atoms that change coordination because that atoms at the boundaries are already bound. It is only at the higher temperatures that there is more of a change so this plot (Figure 5.17) does not plateau as quickly. As at the higher temperature equilibration
there is a large change in the number of atoms that are changing coordination.

Now we focus on the number of atoms with a specific coordination at each temperature and how it differs from the starting structure. The specific number of atoms can be seen in Table 5.6, with the bottom line being the initial structure. The highest percentage

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<td>89.207</td>
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<tr>
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<td>1483</td>
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<td>89.533</td>
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<td>9941</td>
<td>104041</td>
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<td>1.328</td>
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<td>89.633</td>
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<tr>
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<td>447</td>
<td>1.408</td>
<td>8.416</td>
<td>89.576</td>
<td>0.385</td>
</tr>
</tbody>
</table>

Table 5.6: The coordination of the atoms in the bonded polycrystalline structure that range from 1 to 4 at different temperatures. The initial coordination before the simulations is at the bottom of the table.
CHAPTER 5. POLYCRYSTALLINE GRAPHITE

Figure 5.16: Comparison of the grain boundary from the two polycrystalline graphite structures, equilibrated at 300 K. This shows the coordination of all the atoms, with the colours represent the coordination as follows: 1 is blue, 2 is red, 3 is grey and 4 is green. Where (a) is structure I and (b) is structure II.

is again the carbon atoms with a coordination of 3 with almost 90% of the structure in the graphite honeycomb. At 0 K there is no significant change from the initial structure there is only one atom that goes from coordination 2 to a coordination of 4. This is then plotted in Figure 5.18, for a clearer idea of what is happening. This shows an increase in graphitisation with the percentage of atoms with a coordination of 3 becoming larger. Though this percentage difference is lower that what is seen in structure I.

Cascade

The cascades were first simulated at 300 K with the a range of PKA energies from 250 eV to 1000 eV. The PKA was set in the same set of 15 directions as structure I. With the different structure the exact atom that was used as the PKA is different so even though
Figure 5.17: The number of atoms that change coordination at different equilibration temperatures shown with the blue points and produce a trend (red) \( y(x) = 1971 \log(x) - 7280 \).

Figure 5.18: The percentage number of atoms with a coordination of 1 (red) 2 (blue) and 3 (green) change with temperature from the initial structure.

the directions are the same this does not mean it is the same in relation to the orientation of the graphite structures it travels through. An example of the path of the PKA through this new structure is in Figure 5.19.

**Cascade distance**

The average distance that the PKA travels in the cascade at 300 K is written in Table 5.7, with the standard deviation. These distances compared to the other structure are smaller,
Figure 5.19: Section of the bonded polycrystalline graphite cascade with PKA energy 1 keV in the direction of 1 1 4. The structure is rotated to highlight the change in crystal orientation and the path is shown in red.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Av. Distance (nm)</th>
<th>STDEV (nm)</th>
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</thead>
<tbody>
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<td>250</td>
<td>1.49</td>
<td>1.33</td>
</tr>
<tr>
<td>500</td>
<td>2.02</td>
<td>0.80</td>
</tr>
<tr>
<td>750</td>
<td>2.73</td>
<td>0.92</td>
</tr>
<tr>
<td>1000</td>
<td>2.68</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Table 5.7: The PKA’s average distance travelled in simulations at 300 K at different PKA energies. With the range for each of the PKA energies.

This could be due to how the grain boundaries slow down the PKA. There is not much difference and may be this change is only due to the different position of the PKA and not the effect of the grain boundary. For a clearer representation, the PKA distances have been plotted with error bars in Figure 5.20. Just like in the plot in Figure 5.8, the lower PKA energy of 250 eV lies on the graphite trend line. Again this is what is expected as the PKA is less likely to interact with a grain boundary. As the PKA energy increases the distance travelled in the polycrystalline structure II gets further away from the distance travelled in a single crystal graphite. This is the same as that seen in the polycrystalline structure I cascades at this temperature.
Figure 5.20: The average distance travelled for a PKA in the cascade simulations at 300 K in the bonded polycrystalline graphite for different PKA energies. The y-axis error bars show the STDEV of each point, with the red line showing the linear trend of \( y(x) = 0.003259x \) for the polycrystalline structure. The black dashed trend line comes from the 100-1000 eV points from the single crystal graphite cascade.

**Cascade damage**

The damage in these cascades is analysed in the same way as structure I. After the cascade simulation is completed the structure is quenched down to 0 K. This structure also has some movement in the layers, but not as much as the other polycrystalline structure. This means that the count of damage is again only that caused by the PKA, missing any SKA or TKA damage caused.

The average damage over the 15 different directions caused by the PKA are in Table 5.8, with the standard deviation. This shows that the average number of damage is lower in this structure compared with the non-bonded polycrystalline structure. Only at the lower PKA energy of 250 eV is more damage seen. This is even closer to the damage seen in

<table>
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<tr>
<th>Energy (eV)</th>
<th>Av. Damage</th>
<th>STDEV</th>
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</thead>
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<tr>
<td>1000</td>
<td>7.86</td>
<td>2.91</td>
</tr>
</tbody>
</table>

Table 5.8: The average damage produced by the PKA in simulations at 300 K at different PKA energies. With the range for each of the PKA energies.
single crystal graphite which can be seen in the plot of Figure 5.21. The trend in this

![Graph showing average damage vs PKA energy](image_url)

Figure 5.21: The average number of defects caused by the PKA in the cascade simulations at a range of PKA energies. The cascade simulation performed at 300 K and then quenched to find the damage. The y-axis error bars show the STDEV of each point, with the red line showing the trend of $y(x) = 0.2685 \sqrt{x - 108}$ for the polycrystalline structure. The black dashed trend line comes from the high energy PKA damage in the single crystal graphite cascade.

The plot is the square root trend and not linear due to the fact that this is just the damage caused by the PKA. This plot also produces a high TDE but it is lower than the TDE from structure I.

Cascade at absolute zero

To see the damage done by the complete cascade, this structure was equilibrated at 1200 K and then quenched just as structure I was. The PKA atom was also changed to a position similar to the PKA site in the cascades performed on the polycrystalline structure I.

The first thing looked at is the distance travelled by the PKA in these simulations. The average distance over all the directions and the standard deviation are shown in Table 5.9. These are similar to those seen in the same simulations but in structure I. Though at the PKA energy of 500 eV it is lower as there was no significant channelling unlike what was seen in the direction of 1 4 1 and 1 4 4 of structure I.

These distances were plotted in Figure 5.22 and compared to the cascades at 300 K. There is not much difference seen between the simulations done at 300 K and the ones done at 0 K from the high temperature (1200 K) equilibration. There is also no significant difference in the trends from structure I and this one.
Table 5.9: The PKA’s average distance travelled in simulations at 0 K at different PKA energies. With the range for each of the PKA energies.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Av. Distance (nm)</th>
<th>STDEV (nm)</th>
</tr>
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<tbody>
<tr>
<td>250</td>
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<tr>
<td>500</td>
<td>1.46</td>
<td>0.92</td>
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<tr>
<td>750</td>
<td>2.50</td>
<td>1.28</td>
</tr>
<tr>
<td>1000</td>
<td>3.98</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Figure 5.22: The average distance travelled for a PKA in the cascade simulations at 0 K in the bonded polycrystalline graphite for different PKA energies. The y-axis error bars show the STDEV of each point, with the red line showing the linear trend of \( y(x) = 0.003611x \) for the polycrystalline structure. The black dashed trend line is for comparison of the cascade simulations at 300 K.

The damage from these cascades can be counted and not just that from the PKA but the complete cascade. A table of the average number of defects seen and the standard deviation is in table 5.10. These simulation the damage count is higher as now the entire

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Av. Damage</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>500</td>
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<tr>
<td>1000</td>
<td>16.21</td>
<td>3.83</td>
</tr>
</tbody>
</table>

Table 5.10: The average damage produced by the PKA in simulations at 0 K at different PKA energies. With the range for each of the PKA energies.
cascade is counted, it is only at the lower PKA energy were the damage count is similar. This is because at 250 eV the majority of the damage is caused by the PKA or is near its path. These numbers have been plotted in the Figure 5.23. Due to how the cascades are sent, it is only at the high PKA energy of 1000 eV that the PKA really interacts with the grain boundary. So between the PKA energies of 250 eV and 750 eV these simulations are acting like graphite. From the trend of the data in Figure 5.23, using the KP method with $\kappa = 0.8$ this produces a result for the threshold displacement $E_d = 27.2$ eV.

5.4 Discussion

The main consideration in this part of the investigation is counting the defects when the cascades are done at a temperature above absolute zero. A positive aspect out of this is the count of defects only produced by the PKA, showed agreement with the new damage function expressed in Chapter 4.3.

When a count of all the damage produced in these cascades was performed at 0 K it is very clear that the grain boundaries act as a trap for the defects. This has been confirmed in experiments, such as the one done by Thrower [32] where the boundaries act as a sink for the interstitial atoms.

The plot of the two polycrystalline and single crystal graphite together is shown in
CHAPTER 5. POLYCRYSTALLINE GRAPHITE

Figure 5.24: The points that are above the graphite trend line are the simulations with more damage and this is due to the PKA interacting with the grain boundary, creating more damage than what is seen in the single crystal. With the single graphite simulation comparison being at 300 K and the polycrystalline simulations at 0 K fewer defects are seen so the calculated TDE would be higher if a count of the defects could be done from the higher temperature simulations. The two polycrystalline structures have different densities which is a factor contributing to why structure I creates more defects than seen in structure II. As more damage can be created in the higher density grain boundaries.

There are no low energy simulations used to find the TDE in the polycrystalline structure like the ones performed in single crystal graphite. The majority of the structure is made of these crystals which has a value of $E_d = 25$ eV, it is only in the grain boundaries this can potentially change. This could be future work where the PKA is in a grain boundary, these simulations would need to be done in grain boundaries with different angles for tilt and twist.
Chapter 6

Point defect in a (002) twist boundary

In this chapter a DFT-only study on the segregation of an interstitial to (002) twist boundaries was carried out. This work was started for my Masters degree but the calculations have been redone to produce more accurate results. Also the work has been extended to include a comparison with the rotation about an $\alpha$ atom and a $\beta$ atom. The (002) twist boundary was discussed in Chapter 1.4.2.

6.1 Introduction

This section will investigate the observations by Thrower [32] that at 900°C interstitial diffusion becomes isotropic and prismatic interstitial loops only form in (002) twist boundaries. The picture from this Thrower paper can be seen in the previous Figure 1.11 in Chapter 1.4.1 which shows large loops which are the collection of interstitials in the grain boundaries. What Thrower deduced from this image of graphite that is irradiated at a sufficient temperature; is that the grain boundaries act as a sink for the interstitials. Thrower showed the sample had twist boundaries by the images shown in Figure 6.1 of electron diffraction patterns. In Figure 6.1(a) the picture denotes the $AB$ stacked structure of graphite where the diffraction pattern appears as a hexagonal array of single dots. Whereas Figure 6.1(b) shows turbostratic Pyrolytic graphite where that pattern has been smeared into rings by the rotation of different layers. This means that the sample which is shown in Figure 6.1(c) has $5 - 6$ twist boundaries, which can be counted by the dots
Figure 6.1: Pictures from Thrower’s paper [32] of electron diffraction patterns where (a) is a single crystal of \textit{AB} stacked graphite, (b) is turbostratic Pyrolytic graphite and (c) is a thin crystal with 5–6 twist boundaries.
that are grouped together going round in an arc.

The work in this section is to see if calculations can match this deduction. This is done by looking at the energy of the spiro interstitial at example boundaries and comparing them to different environments. This type of study has been done after this work was started with vacancies and the Dienes defect by Ulman and Narasimhan [138].

For the interstitial to gather at the boundaries there has to be migration through the layers, i.e. 3D diffusion. The migration of an interstitial in graphite has been looked at in a few different studies. One such study was Gulans who used the VASP code [139], looking at the three configurations of the interstitial mentioned in Section 1.4.1. Another VASP study was done by Ma [140], looking at the diffusion of an interstitial in graphite. The barrier for the migration was claimed to be lower than 0.5 eV, and the shearing of the layers can reduce this. A DFT study was done using the DMOL3 package and was performed by Zhang et al. [141]. Figure 6.2 from the paper shows the transition states (TS) of the interstitial. These are just a few of the papers which discuss the energy to move from different interstitial positions, going from spiro to spiro through the grafted (bridge) and split (dumbell) interstitial structures. One way to see how the interstitial moves can be seen in Figure 6.3 where two kinds of basal motions are given: rotation about an α–α pair and jumping between α–α pairs. Diffusion through this route would

\[ \text{Figure 6.2: The transition states of interstitials from Zhang [141]. Top left adatom on graphene, top right is the bridge interstitial, bottom left the spiro interstitial and bottom right is the spiro interstitial to the bridge.} \]
be only in the basal direction, but the evidence is that diffusion is more isotropic [34].

In addition the segregation to (002) twist boundaries is taken to imply $c$-axis diffusion is occurring. Latham et al. (private communication) have found a path through the split interstitial which has the same saddle point (transition state) at 2 eV above the ground state for both basal and prismatic diffusion, similar to Zhang’s spiro-spiro path (Figure 6.2).

6.2 Method

Assuming there is a mechanism for 3D diffusion, the next task is to look at these twist boundaries, the structures of which were generated using a code written by J. Boone. The structures comprise of two layers of graphene that are rotated with respect to each other. They can be rotated about an $\alpha$ atom or a $\beta$ atom (these sites are described in Section 1.2). When rotated 60° about an $\beta$ atom then you go from $AB$ stacked graphite back to $AB$ stacked graphite (Figure 6.4(a)), though when rotated 60° about an $\alpha$ atom then you go from $AB$ stacked graphite to $AA$ stacked graphite (Figure 6.4(b)) [142].

When the twist boundaries are optimised an interstitial was added. The structures of the interstitials were described in Section 1.4.1. The interstitial with the lowest formation energy is the spiro-interstitial [36]. The interstitials preferable location is where the two host C-C bonds cross in projection with an angle between $(60-90)°$. The spiro structure as it approaches 90° torsion angle can be seen in the Figure 6.5. The spiro-pentane structure has its minimum at a torsion angle of 90°, so the closer to 90° this angle is the lower the energy. The spiro interstitial in $AB$ stacked graphite is known to be most stable with shearing of the layers [41, 143, 144] which has an energy cost, but in the (002) twist...
boundary the shear energy is zero [145], so it can be assumed shear will occur to align the layers optimally for the spiro interstitial in the (002) twist boundary.

## 6.3 Results

The results come from the optimisation of the 14 graphite structures with different relative rotation angles (RRA) [54] and the $AB$ stacked and the $AA$ stacked graphite, with and without interstitial. The total energy of these structures were produced using the AIMPRO code mentioned in Section 3.4 and were used to find the standard heat of formation for these structures. The Gaussian basis set used was $pdpp$, the Brillouin zone is sampled with
the Monkhorst and Pack scheme, and the states are occupied according to the first-order Methfessel-Paxton scheme with $kT = 0.01$ eV.

The 15 RRA are listed in Table 6.1 starting at $AB$ stacked graphite $0^\circ$ and ending at $60^\circ$ which is either $AB$ or $AA$ stacked graphite depending on whether it is rotated about a $\beta$ or an $\alpha$ site. The number of atoms is given for each RRA, one RRA is given twice (38.21$^\circ$) as the initial structure of 28 atoms was too small. A larger cell was created that was 112 atoms, allowing more potential sites for the interstitial.

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<th>No. atoms</th>
</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>60.00</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 6.1: The number of atoms in each RRA cell.

(38.21$^\circ$) as the initial structure of 28 atoms was too small. A larger cell was created that was 112 atoms, allowing more potential sites for the interstitial.

6.3.1 Formation energy

The standard heat of formation (STHOF) [141] of the rotated structure compared to the $AB$ stacked graphite is calculated using equation (6.1). Also compared to the $AB$ stacked graphite is the $AA$ stacked graphite. Where $E_F$ is the STHOF energy, $E_H$ is the total energy of the host structure, which is compared to perfect $AB$ stacked graphite total
energy ($E_P$) and $n$ is the number of atoms in each structure.

$$E_F = \frac{E_H}{n_H} - \frac{E_P}{n_P}$$  \hspace{1cm} (6.1)

This comparison of rotated structures about an $\alpha$ and a $\beta$ site with $AB$ stacked is plotted in Figure 6.6. The rotation about an $\alpha$ site is in Figure 6.6(a) and the rotation about a $\beta$ site is in Figure 6.6(b). These plots match the ones from Campanera’s DFT calculations.

![Figure 6.6](image)

(a)

![Figure 6.6](image)

(b)

Figure 6.6: The standard heat of formation energy difference between the $AB$ stacked structure and the different relative rotation angle (RRA). (a) is rotated about an $\alpha$ atom and the trend line in red is a parabolic line $[2.38 \times 10^{-3}(RRA)^2 - 1.43 \times 10^{-1}(RRA) + 7.62]$ meV and (b) is rotated about a $\beta$ atom and the trend line in red is a parabolic line $[1.54 \times 10^{-3}(RRA)^2 - 9.25 \times 10^{-2}(RRA) + 6.97]$ meV. For both trend lines the points $RRA = 0^\circ$ ($AB$ stacked) and $RRA = 60^\circ$ ($AB \& AA$ stacked) are not included.
on Moiré patterns on graphite [54] also based in AIMPRO. Showing a relationship with the relative rotation angle and the formation energy as well as AA stacked graphite requires a higher energy than that of AB stacked graphite.

The standard heat of formation of a spiro interstitial in a twist boundary was then calculated using equation (6.2). Where +1 means the structure is with an interstitial.

\[ E_F = E_{H+1} - E_H - \frac{1}{n_P}E_P \]  

(6.2)

For each RRA structure the interstitial was placed in three different sites so three formation energies for a spiro-interstitial were calculated using equation (6.2) for all of these structures. A graph was produced for the standard heat of formation for an interstitial versus the relative rotation angle (RRA) shown in Figure 6.7. This produced a similar trend to the graph of the relative formation energies of the relative rotation structures versus their RRA.

Both graphs seen in Figure 6.7 have a parabolic trend that is symmetric about the 30° RRA. When plotting the fit in both plots, the points in red were not used. This is because in general RRA of 0° and 60° are discontinuities and the red points are departures from the spiro structure. The point on the RRA = 0° has a large formation energy due to the fact it was the grafted not the spiro structure. The red points on the RRA = 60° in Figure 6.7(a) were from the AA stacked structure. In Figure 6.8 you can see the structures of the defects formed, the higher energy being a spiro interstitial but with a torsion angle of 0° seen in Figure 6.8(a). The lower energy defect is the y-lid structure seen in Figure 6.8(b).

6.3.2 Segregation

The lowest of the three formation energies for each structure were then compared to the AB stacked case and plotted (Figure 6.9). There is still a parabolic trend, the points are also symmetrical about 30°, so each data point appears at θ and 60° - θ. The structure is rotated 60° about a β atom which produces the AB stacked structure.

There is clear evidence in Figure 6.9 of energy lowering in all twist boundaries and thus that interstitials will migrate from AB stacked graphite to the twist boundaries. This matches the experimental results from Thrower [32].
Figure 6.7: Standard heat of formation energy for interstitials in (002) twist boundaries with different relative rotation angle (RRA). The red points are not spiro interstitials but other types of interstitials. (a) starts at 0° which is the AB stacked graphite and finishes at the AA stacked graphite with a RRA of 60° as it is the rotation about an α atom. The graph has a symmetry about 30°, the parabolic fit is \[3.78 \times 10^{-4}(RRA)^2 - 2.27 \times 10^{-2}(RRA) + 5.43\] eV. (b) starts at 0° which is the AB stacked graphite and finishes at the AB stacked graphite with a RRA of 60° as it is the rotation about an β atom. The graph has a symmetry about 30°, the parabolic fit is \[4.14 \times 10^{-4}(RRA)^2 - 2.48 \times 10^{-2}(RRA) + 5.38\] eV.

6.3.3 Torque

Looking at the projection of the two host bonds onto the basal plane, the angle between them is taken as the ‘torsion angle’. After the structure has been geometrically optimised, this angle becomes approximately the same for each RRA, for the best sites. There seems
CHAPTER 6. POINT DEFECT IN A (002) TWIST BOUNDARY

Figure 6.8: The defect structures from the AA stacked graphite where (a) is the spiro structure with a torsion angle of 0° and (b) is the y-lid interstitial defect.

Figure 6.9: The standard heat of formation energy difference between the AB stacked structure and the different relative rotation angle (RRA) for the spiro interstitial. The trend line is a parabola \(4.79 \times 10^{-4}(RRA)^2 - 2.88 \times 10^{-2}(RRA)\) meV that goes through the origin.

to be a linear relationship between the standard heat of formation and the torsion angle (Figure 6.10). When the interstitial is not placed such that the torsion angle is equal to or greater than 60° then the formation energy is higher than the other values calculated for the same structure. Looking at the lowest formation energy for each of the different RRA, the torsion angle for the bonds from the spiro interstitial were measured. The values can be seen in the Table 6.2, the first angle is 0.0° which is from the interstitial in AA stacked graphite and is highest in energy because the interstitial carbon is forced to be planar and four-coordinate. The values from Table 6.2 are plotted and produce a straight line trend seen in the plot in Figure 6.10. This trend could be due to the torque produced from the
Figure 6.10: The formation energy of each interstitial compared with the torsion angle after optimisation. There is a straight line trend \([-0.024x + 6.902]\) eV, where the gradient gives the torque on the system.

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<thead>
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Table 6.2: The standard heat of formation energies for different bond angle interstitial sites, to show the torque on the supercell.
spiro interstitial in the structures. The origin of the torque is from the spiro structure minimum being at a torsion angle of 90°. The gradient from the graph in Figure 6.10 is shown in equation (6.3) which produced a value for torque $\tau = 0.023$ eV deg$^{-1}$.

$$\tau = -\frac{dE}{d\theta}$$  \hspace{1cm} (6.3)

Another way to look at the torque acting on the system is from the segregation plot in Figure 6.9. This method involves looking at the gradient at the beginning of the slope from either the down or up side, due to its symmetry. This produces a value from equation (6.3) for $\tau = 0.019$ eV deg$^{-1}$ in AB stacked graphite. So this leads to the spiro interstitial producing a torque:

$$\tau = (21.5 \pm 2.5)x10^{-3} \text{ eV deg}^{-1}$$

6.4 Discussion

This section shows that graphite with a spiro interstitial prefers to lie in a twist boundary compared to the perfect AB stacked graphite. When the interstitial is in AB stacking it tries to make the layers shear and its energy is pushed up by the requirement that the host bonds are at 60° to one another. In a twist boundary, the closer the RRA is to 30° the more stable the spiro interstitial will be that binds the layers together. In exploring sites for the spiro interstitial other interstitial structures formed; for example the y–lid interstitial which has a higher formation energy. This confirms that the spiro interstitial is the most stable of the interstitials in a graphite structure. If the defect density is too high the formation energy is lower even with the same structure, which can be seen from the structures with a RRA of 24.43° and 33.99°, with the $RRA = 38.21°$ initial structure too small for more than one site for the interstitial. The torsion angle needs to be in the range of (60–90)° for the spiro structure to be obtained and optimised. This can be seen when the angle is 50° for the graphite structure with a RRA of 15.18°, and how much higher its formation is compared to the other structures with that RRA.
Chapter 7

Conclusion

At the end of each chapter there is a discussion which summarises the findings for that section. This chapter will be a summary of all these findings.

Graphite is used as a moderator in the UK’s nuclear reactors, where it is bombarded with fast neutrons that cause damage. Molecular dynamic simulations were run to show what is happening to the graphite that is being irradiated. These simulations were performed using the EDIP and ZBL potentials, to simulate thermal spikes and cascades. These potentials were also used to calculate the energy of point defects, but for a more accurate calculation \textit{ab initio} was used. These \textit{ab initio} calculations were run using AIMPro, and focused on the migration of the interstitial into grain boundaries.

The thermal spike simulations in single crystal graphite show very little defect formation even in the higher ranges of energy. With the high amount of energy going into each layer, graphite shows a high resilience to amorphisation. This means that graphite produces very little damage when the PKA travels through the graphite before collisions occur (swift heavy ion-like behaviour). The main defect that is formed in these simulations is the intimate Frenkel pair. Other carbon structures were also simulated and showed how unique graphite is due to its layered nature.

A highlight from the amorphous carbon simulations was the area of the thermal spike effect on the bond order. This showed the possibility of the thermal spike being able to heal some of the damage created in the graphite moderator. Thermal spikes were also performed on defective graphite. These simulations showed defect motion at the higher energy, confirming thermal spikes’ ability to heal defected graphite.

Cascades in the single crystal graphite are also unique, and they do not behave in
any way like the other carbon structures simulated. In diamond a shock wave travels through the structure but with graphite the PKA passes through the layers causing very few defects to be formed. There is also the possibility for channelling which is where the PKA travels through the graphite without colliding with other atoms. The defects that are formed in graphite at the end of these simulations are generally the same as the structures seen in DFT studies, though there are some differences such as the structure of the spiro interstitial and also the appearance of the sp$^3$–sp$^3$ link defect.

The single crystal graphite cascade simulations created more damage than seen at the end of the thermal spike simulations. The simulations show that the damage produced is directionally dependent and that the most damage in these simulations happened at the end of the cascade. In many cases the divacancy structures seen at the end of the trajectory, lead to the potential of directly nucleated extended defects.

The cascades were initiated at higher and lower PKA energies. With the lower PKA energies the focus was on the threshold displacement energy and new damage function was formulated. $E_d$ was calculated a variety of ways at different temperatures with a final value was $E_d \approx 25$ eV at 300 K. A new damage function for calculating the number of defects created was put forward (equation (7.1)).

\[
N_d = \begin{cases} 
0 & 0 < \epsilon < 1 \\
\kappa \sqrt{\epsilon - 1} & 1 < \epsilon < 2 \\
\frac{\kappa \epsilon}{2} & 2 < \epsilon 
\end{cases} \tag{7.1}
\]

This new function was further broken down into contributions from PKA’s, SKA’s and TKA’s (equation (7.2) and equation (7.3)) taking into account the difference between the PKA and SKA’s ability to create damage.

\[
f_m(\epsilon) = \begin{cases} 
0 & 0 < \epsilon < 2m - 1 \\
\kappa_m \sqrt{\epsilon - (2m - 1)} & 2m - 1 < \epsilon 
\end{cases} \tag{7.2}
\]

\[
N_d = f_1(\epsilon)(1 + f_2(\epsilon))(1 + f_3(\epsilon)) \tag{7.3}
\]

This new formula was justified by undertaking cascade simulations starting from an interstitial, to reproduce behaviour of knock-ons after the PKA (SKA, TKA, etc.).

Then the question of the validity of EDIP for these simulations was addressed by comparison with DFT calculations. The formation energy values for interstitials using
EDIP are higher than the DFT calculated values but the energies for the vacancies are lower. Considering that EDIP was created for simulation of amorphous carbon the values achieved with energy minimisation producing values comparable to DFT calculations is encouraging.

The cascade simulations were also done with a polycrystalline graphite structure. There were two types of structure: the first had dangling bonds at the grain boundaries and the second the grain boundaries were bonded. More damage is seen at the end of the simulations in polycrystalline graphite compared to single crystal graphite. This is due to the fact that the grain boundaries act as traps for the PKA. When the PKA travels through the grains it is slowed down faster than in the structured section of graphite. So the polycrystalline structure of graphite experiences smaller cascades of damage in length terms but more damage is produced.

The last section shows that graphite with a point defect of a spiro interstitial prefers to be in a graphite structure with a twist boundary compared to the perfect $AB$ stacked graphite. When the interstitial is in the $AB$ stacked it tries to rotate and shear the host structure, which will explain for some of its higher energy. The closer to 30° for the RRA of the graphite structure the more stable the spiro interstitial will be that binds the layers together. This means that the spiro interstitial in an (002) twist boundary is the most stable of the interstitials in a graphite structure which matches the deductions in literature.
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