Atomistic Simulations of Materials for Nuclear Fusion

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Declaration of originality: The work presented herein is my own, with contributions from others appropriately referenced and acknowledged.

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Abstract

Nuclear fusion has held the promise of unlimited clean energy for over fifty years. However, owing to the technical challenges of achieving a sustained reaction, this promise remains unrealised. Chief among these challenges is the survivability of reactor materials, which are subject to extreme temperatures and flux of fast neutrons. To aid in understanding damage processes, atomistic simulations have been employed to model the fundamental processes of radiation damage, with some models validated by comparison to inelastic neutron scattering results.

Beryllium rich beryllides, in particular the Be\textsubscript{12}M materials (where \(M\) is a transition metal), are under consideration for neutron multiplying applications in fusion reactors, however the basic properties of some of these materials remain poorly characterised. Herein, DFT simulations have been used to clarify the structure of Be\textsubscript{12}Ti, which was previously in contention. Further, several basic properties of Be\textsubscript{12}Ti have been predicted, including the thermal expansion, bulk modulus, elastic constants and lattice parameters.

The phonon density of states of Be\textsubscript{12}M (\(M=\text{Ti/V/Mo/Ta/Nb}\)) and Be\textsubscript{13}Zr have been predicted, with trends observed based on the mass of the \(M\) species. Inelastic neutron scattering has also been performed, and results compared with the simulated phonon density of states. The experimental results were significantly broadened, making analysis difficult. It was found that signal at low energies is attributed to second order
reflections, and has better energy resolution than the first order data. When simulated
results are artificially broadened, they bear strong qualitative resemblance to exper-
imental results for all materials.

Point defects including vacancies, interstitials and antisite defects were investigated in
Be$_{12}M$ materials ($M=$Ti,V,Mo,W) using DFT, with interstitial sites identified for the
first time. Beryllium defects are consistently more favourable than transition metal de-
fects. Schottky disorder is the lowest energy intrinsic disorder process in all materials,
although beryllium Frenkel is comparable for Be$_{12}$Ti and Be$_{12}$V. Small defect clusters
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Be$_3$Be$_3$ formation is almost always unfavourable, and $V_{M}V_{M}$ is always unfavourable.
Non-stoichiometry is extremely limited, to the extent that these intermetallics may be
considered line compounds. Migration is predicted to be dominated by $V_{\text{Be}}$ mediated
processes and to be weakly anisotropic.

Low energy displacement simulations using empirical potentials were performed for
beryllium, tungsten, carbon and tungsten carbide. Displacement was predicted to
be strongly dependent on the potential used, as well as the local environment of the
displaced species. For beryllium, tungsten and diamond, defect recovery is predicted
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threshold displacement energy. The threshold displacement energy is a strong function
of crystallographic direction for all materials. New models have been developed to
predict the maximum displacement as a result of a displacement event.
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Chapter 1

Introduction

1.1 The Nuclear option

Throughout history, the combustion of organic matter has been used to generate useful energy. Initially, it was used to cook food, for heat and for light. Eventually, the discovery that heat could be converted to mechanical work ushered in the industrial revolution, replacing hundreds of workers with the noisy clack of steam powered looms and machining plants. As a consequence, demand for fuel became insatiable. Wood and other plant materials were no longer enough, leading to the rise of fossil fuels: first coal, and then oil and gas.

In essence, little has changed since then. Though energy is now distributed by means of an electrical grid, for the most part it is still generated by burning fossil fuels. During the first quarter of 2014, 82.0% of the world’s primary energy supply came from fossil fuels [1].

The continued use of fossil fuels on such a large scale has a devastating impact on
the world’s climate. The concentration of carbon dioxide, a potent greenhouse gas, in the atmosphere has increased from an average of 280 ppm during the pre-industrial era to an average of 425 ppm in 2016 [2, 3]. With it, global temperatures have risen precipitously, 2010 being 0.87 °C warmer than the preindustrial average and current climate models predicting a rise of 1.4 - 5.8°C by 2100 [4, 5]. In addition, the particulate matter released from the incomplete combustion of fossil fuels is estimated to contribute to the premature deaths of 3 million people annually, the majority of these occurring in developing and rapidly industrialising countries such as India and China [6].

Due to these calamitous effects there is a global effort to shift to low carbon energy sources; either renewable or nuclear energy. Renewable options principally consist of hydro, wind and solar. Excluding hydro, which makes up the bulk of renewable electricity generation, but has limited capacity for expansion, renewables in 2014 constituted 6.3% of global electricity production [1]. Encouragingly, renewable energy production (excluding hydro) increased by 20% in 2015. It should however be noted that in absolute terms this is less than the increase in fossil fuels over the same period [7]. While there have been great strides in reducing the cost of these technologies, significant barriers remain to their widespread implementation. The capacity factor of wind and solar is strongly dependent on local climate, rendering them inappropriate for some countries and locations. In addition, these technologies generate energy intermittently, necessitating the use of either energy storage or additional load following generating capacity, which is most often provided by fossil fuels.

Nuclear energy is a somewhat contentious alternative. Currently it delivers 21% of the UK electricity demand and 11% globally [8, 9]. Like renewables it is a low carbon technology, however unlike renewables it produces a constant baseload electricity supply and can be built anywhere a large water source can be used as a heat sink. Post
Fukushima-Daiichi however, attention has been refocused on the perceived safety risks of nuclear energy, which has eroded public confidence in the technology, most notably in Western Europe where several countries have chosen to phase it out altogether. Nuclear fusion may offer an alternative that can provide a continuous baseload of energy without the perceived safety risks of conventional nuclear power and greenhouse gas emissions of fossil fuels. However, to achieve this, significant scientific and engineering challenges need to be overcome. These will be explored in this thesis.

### 1.2 Fusion and Fission

All nuclear energy is derived from the binding energy between nucleons in an atom. The magnitude of this energy is dictated by the balance between the strong nuclear force which binds the nucleons together, and the repulsive electrostatic interaction which mutually repels the positively charged protons. This leads to the iconic binding energy per nucleon curve reproduced in figure 1.1. Analogous to the shell structure of electrons around an atom, nuclei also have an internal structure, with full shells of both protons and neutrons resulting in more stable isotopes. This is particularly evident for light elements such as $^4$He and $^{12}$C which both have filled protons and neutron shells, and thus are significantly more stable than other isotopes of similar atomic number [10].

The effect of the nuclear shell structure notwithstanding, from figure 1.1 it is apparent that there is a clear trend towards higher binding energy for moderately sized nuclei. For light elements such as hydrogen, it is generally energetically favourable to fuse two together to form a more massive one, up to the most stable nuclei, $^{62}$Ni (commonly misquoted as $^{56}$Fe) [10]. For more massive elements such as uranium and plutonium, it is energetically favourable to fission them into two smaller nuclei. These two processes,
fusion and fission, are the two principal nuclear reactions that can be used to generate energy.

It is worth noting that the binding energy of nucleons in a nucleus is several orders of magnitude higher than that which binds valence electrons to an ion. Consequently, nuclear reactions on average release around a million times more energy than chemical reactions.
1.3 Fission

In practice, fission is somewhat easier to achieve than fusion and thus forms the basis of all current nuclear power. The most common fission reaction for nuclear power is that of $^{235}\text{U}$ (although $^{233}\text{U}$ and $^{239}\text{Pu}$ are also used) [11], an example of which is

$$n + ^{235}\text{U} \rightarrow ^{141}\text{Ba} + ^{92}\text{Kr} + 3n \quad (1.1)$$

In this reaction, a neutron causes the fission of the $^{235}\text{U}$, releasing three neutrons and forming the fission products $^{92}\text{Kr}$ and $^{141}\text{Ba}$. The total energy released is 202.5 MeV, from the discrepancy in binding energy of the nucleons between the reactants and products. A wide range of fission fragments can be formed in this way; typically with a two-thirds to one-third ratio in atomic number, as shown in the fission fragment yield for $^{235}\text{U}$ presented in figure 1.2a [12]. Due to the stable ratio of neutrons-protons being higher for heavier isotopes, as shown in figure 1.2b, many fission fragments are unstable and undergo a beta-decay chain with a short half-life.

As more neutrons are released than absorbed in a fission reaction, it is possible to sustain a chain reaction simply by bringing enough fissile material together so that most of the released neutrons go on to cause another fission reaction. In addition to fissile elements such as $^{235}\text{U}$, power reactors usually include a significantly higher proportion of a fertile isotope, that is an isotope which can capture a neutron to become fissile [11]. In the case of uranium this is usually $^{238}\text{U}$, which makes up 99.3% of natural uranium and is difficult to separate from $^{235}\text{U}$ [13]. $^{238}\text{U}$ has a much lower fission cross-section (except in the MeV incident energy range), although it does have a moderate neutron capture cross-section across all energies [14]. When $^{238}\text{U}$ captures a neutron, it becomes $^{239}\text{U}$ which rapidly undergoes beta decay to $^{239}\text{Np}$ and then $^{239}\text{Pu}$. $^{239}\text{Pu}$ is fissile (indeed it is a fissile material used in atomic weapons) which means it can be
1.3. Fission

Figure 1.2: a) Average fractional fission yield of $^{235}$U when bombarded with a thermal neutron. Data from [12]. b) stability of isotopes plotted as a function of atomic number and number of neutrons. $^{235}$U and its fission products highlighted in black. Data from [13].

used as fuel. Thus a higher proportion of natural U can be utilised rather than only the small amount of $^{235}$U. Occasionally, however, $^{239}$Pu can capture a neutron without undergoing fission, transmuting to $^{240}$Pu, which by the same mechanism can become $^{241}$Pu and then $^{242}$Pu [13]. These isotopes are unstable with half-lives on the order of $10^5$ years, usually initiating an alpha decay chain to more stable isotopes such as lead [13].

Light Water Reactors

The most common type of nuclear power reactor is the Light Water Reactor (LWR). The LWR has two main variants; the Pressurised Water Reactor (PWR) and the Boiling Water Reactor (BWR), a schematic of which is presented in figure 1.3. Such reactors account for 89 % of nuclear power production worldwide [11].
These reactors use UO$_2$ fuel which is chosen as it has a high melting temperature, good thermal stability and can accommodate a wide range of fission products [15]. The reactor is cooled with water at a pressure of approximately 16 MPa and temperature around 315$^\circ$C [15]. In a BWR, the cooling water is converted into steam directly inside the core, which is then used to turn a turbine, whereas in a PWR it is used to generate steam externally. Water also acts as a neutron moderator, in which neutrons undergo elastic scattering interactions with hydrogen nuclei. This slows the neutrons down to thermal velocities where $^{235}$U has a higher fission cross-section. Reactivity, and by extension power output, is primarily controlled through the insertion and removal of control rods which contain a neutron absorbing material, typically $^{10}$B. In addition, two important negative reactivity feedback loops; thermal expansion of the fuel and moderator, cause the reactivity to decrease as temperature increases, leading to very stable power output [16].
1.3. Fission

Safety Concerns

While the LWR design has been extremely successful, it has been shown to be susceptible to Loss of Coolant Accidents (LOCA), which have the potential to cause dispersal of radioactive material. The susceptibility of these reactors to this type of accident is due to the decay of fission products and higher actinides, which immediately after reactor shutdown generate around 6% of the heat from full power operation [16]. For a typical PWR which generates 4 GWt at full power, this is on the order of 250 MWt. This is too much heat to remove from the reactor core via radiative and convective losses should active cooling be compromised. Thus, without intervention, the temperature of the core increases until it surpasses the melting point of the fuel. If this occurs, it may lead to energetic dispersal of the fuel which has the potential to breach the containment, particularly where the fuel is clad with zircalloy which, at elevated temperatures, reacts violently with steam to produce hydrogen. Release of radioactive fission products and higher actinides from the fuel into the environment can have serious negative health consequences to the surrounding population, particularly as some isotopes ($^{131}$I, $^{137}$Cs and $^{90}$Sr) accumulate in biological tissues [17]. Further, as some of these isotopes have long half-lives, this can render areas uninhabitable for generations [18].

The possibility of such accidents was brought into sharp focus by the Three Mile Island incident in 1979, in which a faulty valve allowed a large amount of coolant to escape leading to a partial meltdown of the core [17]. Public opinion of nuclear power, already tainted by its association with nuclear weapons, became significantly less favourable due to perceived safety concerns, despite very little radiation being released. This was compounded by the Chernobyl disaster in 1986, which, although not a LWR in the usual sense, demonstrated the potential risks to wide segments of the population, with
thousands of square kilometres evacuated and a clean-up effort (which continues today) running to billions of USD [17]. These events greatly slowed the uptake of new nuclear reactors, as shown in figure 1.4. More recently, the partial melt down at the Fukushima Daïichi plant following the earthquake of 2011 led to a drop in public support for nuclear power and subsequently the mothballing of the entire Japanese nuclear fleet and the phase out of nuclear fission in several European countries [17].

Figure 1.4: Total capacity in GWe and total number of commercial power reactors globally throughout the late 20th and early 21st century. Well publicised nuclear accidents are highlighted. Data from [19].

The nuclear industry has responded to the negative public perception of nuclear safety by adding multiply redundant and divergent safety systems to nuclear reactors which has significantly increased capital and overall costs. Further, it could be argued that the strict safety culture around nuclear power has inhibited the development and adoption of other types of reactors which may potentially be safer and more economical than PWRs and BWRs. Aside from safety, waste is also a key issue. Given the isotopic
1.4 Fusion

In principle, nuclear fusion does not have the same issues with safety or waste as nuclear fission, but maintains the key advantage of producing low carbon, continuous baseload power. The only waste product is stable $^4\text{He}$, precluding the risk of a meltdown and not requiring storage, although some reactor materials may be activated. As such, it enjoys much greater public support than conventional fission power [22].

The most promising reaction for nuclear fusion power is the deuterium-tritium reaction;

$$^2\text{D} + ^3\text{T} \rightarrow ^4\text{He}(3.5\text{MeV}) + n(14.1\text{MeV})$$  \hspace{1cm} (1.2)

although several others have been proposed. In this reaction, two isotopes of hydrogen are fused to produce $^4\text{He}$ and an energetic neutron. This reaction has a relatively low activation energy, dictated by the Coulomb repulsion between the two positively charged nuclei (which scales with atomic number) and high energy release per nucleon as demonstrated in figure 1.1. Relative to the Coulomb interaction, the strong nuclear force which binds nuclei together operates over much shorter length scales. Thus, to achieve fusion, two nuclei must be brought close enough together that the strong nuclear force overpowers the coulomb repulsion. In practice, this is usually achieved...
1.4. Fusion

by maintaining extremely high temperatures and densities in the fuel, resulting in it
becoming a plasma.

1.4.1 Lawson Criteria and the Triple Product

To maintain the temperature, and thus nuclear fusion, any reactor must generate more
energy than is lost to the environment. This is laid out explicitly in the Lawson criteria
which defines the conditions necessary to achieve ignition, that is to say a self-sustained
fusion reaction, of a fuel plasma as an energy balance [23]:

\[ P = \eta \times (P_f - Q) \] (1.3)

where \( P \) is the net power of the device, \( \eta \) the efficiency, \( P_f \) the power from fusion and \( Q \)
the energy loss per unit time. Clearly, as the energy loss approaches the energy released
through fusion then the power tends to 0. One of the key aims for a fusion reactor
then, is to lower \( Q \) such that fusion can be maintained. As mentioned previously, the
fusion power \( P_f \) is dependent on the temperature of the plasma. More specifically the
energy density can be estimated using the Maxwell-Boltzmann [24] distribution as:

\[ \frac{dP_f}{dV} = \frac{1}{4} en^2 \langle \sigma_F(T)v \rangle \] (1.4)

where \( v \) is the relative velocity, \( e \) the energy/reaction, \( n \) the number density of the
reactants, \( \sigma_F(T) \) the fusion cross-section as a function of temperature and \( \langle \rangle \) denotes
an average over the Maxwellian velocity distribution at that temperature. For devices
that operate in a steady state configuration, it is useful to think of the problem in
terms of the ratio of energy lost to total energy density \( W \), also known as the energy
1.4. Fusion

confinement time, \( T_E \),

\[
T_E = \frac{W}{Q} \tag{1.5}
\]

This can be rearranged to find \( Q \), and \( W \) calculated using Boltzmann statistics to give

\[
Q = \frac{3nk_BT}{T_E} \tag{1.6}
\]

which, when substituted into the original statement of the Lawson criterion (ignoring the efficiency term) along with the equation for \( P_f \), returns the conditions necessary to achieve ignition in terms of \( T_E \)

\[
nT_E = \frac{12}{e} \frac{k_BT}{\langle \sigma_F(T) \rangle v} \tag{1.7}
\]

Thus, the minimum product of reactant density and confinement time can be calculated as a function of temperature. Most fusion reactor concepts (which are explored in detail in section 1.4.2) can attain a maximum pressure \( p \), but vary the density and temperature of the fuel. In this case, assuming the ideal gas equation holds and thus \( p \propto nT \), it is useful to express the Lawson criteria in terms of the triple product

\[
nT_E T = \frac{12}{e} \frac{K_BT^2}{\langle \sigma_F(T) \rangle v} \tag{1.8}
\]

The \( nT_E T \) which satisfies the Lawson criteria is presented as a function of temperature for the T-T and D-\(^3\)He (which is considered for fusion as it is aneutronic) reactions in figure 1.5. It can be seen the \( nT_E T \) required to achieve ignition is minimised at finite temperature. This is due to the microscopic fusion cross-section falling off at higher energies along with increasing radiative losses. It is clear that the D-T reaction has the lowest minimum triple product of the two reactions, which is why it is considered the best prospective fuel for a fusion reactor. The D-T minimum occurs at around 150 million kelvin which is thus the target for devices attempting to generate fusion energy.
1.4. Fusion

1.4.2 Achieving Fusion

To satisfy the Lawson criteria laid out in section 1.4.1 and thus achieve fusion power, a number of approaches have been explored. Inspiration was first taken from nature, as it was theorised in the 1920’s that fusion is the energy source of stars, based on the total mass discrepancy between hydrogen and helium. Indeed, in our sun hydrogen is fused into helium through the proton-proton chain [26, 27]:

\[ ^1H + ^1H \rightarrow ^2D + \beta^+ \] (1.9)

\[ ^2D + ^1H \rightarrow ^3\text{He} \] (1.10)

\[ ^3\text{He} + ^3\text{He} \rightarrow ^4\text{He} + ^2\text{H} \] (1.11)

The core of the sun has a maximum temperature of approximately 15 million kelvin [28], and further reaction 1.9 has a very low reaction cross-section due to the conversion of
a proton to a neutron. As such, at first glance it would seem unlikely that the Lawson criteria could be met. Fusion is however sustained by the extremely high density of the core (in excess of 150000 kg m$^{-3}$ [28]) and extremely long confinement time. Despite this, the average energy release per unit volume of the core is only 276.5 W m$^{-3}$ [29], significantly less than the metabolism of an adult human. Given the overwhelming size of the sun, this is enough to maintain the conditions for fusion to occur. It is obvious however, that this approach is impractical for terrestrial fusion devices.

![Figure 1.6: The sun. Image credit NASA.](image)

Fusion was first achieved in a laboratory in 1932 by bombarding targets of deuterium, tritium and $^3$helium with deuterium nuclei using a particle accelerator [30]. Such a device requires much more energy than is released, and thus is not a practical solution for fusion power.

Fusion remained a curious aside with no practical application until the advent of the Manhattan project during World War Two. The aim of this project was to develop the first nuclear fission bomb, an endeavour which was successfully concluded with the Trinity test in 1945 [17]. Early in the project, it was theorised that the detonation of
a conventional fission weapon could be used to achieve the temperature and pressure required to ignite a fusion reaction, thus significantly boosting the yield of the weapon. Work began on developing this concept, which continued throughout the Manhattan project and accelerated with the onset of the Cold War. It culminated in the detonation of the first “boosted fission weapon” (in which only a small portion of the energy released comes from fusion) in 1950 [31], and then the first true thermonuclear bomb, Ivy Mike in 1952 [17]. In these devices, a primary fission detonation is used to release energy and neutrons which are focused on the fusion fuel. This fuel is surrounded by a dense material (which may itself be fissionable) such that when this energy is focused upon it, it collapses with enough inertia to compress and heat the fusion fuel to induce fusion.

In parallel with this, work began on developing fusion for civil energy production. This presented an additional problem to that of developing a weapon: how to contain the fuel which, by necessity, must be at millions of kelvins? In the case of a weapon, containment is only briefly achieved with an imploding mass of $^{238}\text{U}$. A civil reactor however must operate in a (quasi)continuous state. This problem has aptly been likened trying to create a “Sun in a bottle”; clearly no material could withstand such temperatures and pressures, thus other means of containment are required, which isolate reactor materials from direct contact with the plasma. Two main approaches were developed: Inertial Confinement (ICF) and Magnetic Confinement (MCF).

**Inertial Confinement Fusion**

From the perspective of fusion power, the most successful ICF concept has been laser inertial confinement [32]. In this approach, several high powered lasers are focused on a small pellet of fusion fuel for a very short time, causing the surface to rapidly
vaporise creating a high pressure shockwave, compressing and heating the centre of the fuel pellet to fusion conditions, as shown in figure 1.7.

![Diagram of NIF target capsule ignition sequence]

1) 192 UV laser beams rapidly deposit 1.85 MJ of energy in the inner surface of the Hohlraum
2) X rays from the Hohlraum vapourise the surface of the capsule generating explosive blowoff, heating and compressing the D-T fuel
3) The D-T fuel reaches temperatures and densities sufficient to initiate fusion

Figure 1.7: Ignition sequence of a NIF target capsule. Adapted from [33].

The most recent incarnation of this concept is the National Ignition Facility (NIF), which is used to test materials for the U.S. thermonuclear weapons stockpile. The device was originally designed and predicted to achieve ignition [34], however this has not been achieved. Earlier attempts at laser ICF underperformed due to unpredicted nonlinear optic effects at high laser power, although these issues had already been addressed at the conception of NIF [35]. Instead, it appears that hydrodynamic instabilities in the outer layers of the target capsule, in particular Rayleigh-Taylor instabilities, prevent the fuel from reaching the conditions necessary for ignition [35]. These unpredicted issues have cast doubt on the feasibility of this approach to generate fusion energy.

**Magnetic Confinement Fusion**

MCF, the other key confinement approach, uses magnetic fields to confine a plasma of the fuel. Plasmas are electrically charged, and as such subject to the Lorentz force
(equation 1.12). Thus, when a current is passed through them in the presence of a sufficient magnetic field they can be contained. The first of these devices was the Z-pinch, developed from 1946 onwards, which uses a simple cylindrical reactor with a magnetic coil around the centre. When an electrical current is applied to this coil, it exerts a force,

\[ F = qE + qV \times B \]  

(1.12)
on the fuel plasma within, compressing and heating it [36]. While such devices were a useful proof of concept, sustaining fusion was found to be impossible due to instabilities in the plasma [36]. They did, however, provide the inspiration for more successful devices operating on similar principles such as the Stellerator and the Tokomak, the latter of which has been perhaps the most successful type of fusion reactor to date. The Tokomak confines a ring of plasma using helical magnetic fields, which are generated using a combination of a toroidal and poloidal field. The toroidal field is generated by passing a current through the plasma and the poloidal field using electromagnets surrounding the torus, as represented in figure 1.8 [37].

Figure 1.8: Magnetic fields and electrical currents in a section of a conventional tokomak device.
1.4. Fusion

The confined plasma is heated through a combination of ohmic heating, neutral beam injections and radio-frequency heating. These devices have been able to hold a mostly stable plasma, although some serious instabilities in the plasma do occur, ranging from global disruptions which can quench the plasma to localised edge disruptions which impinge on the reactor wall but do not lead to discharge of the plasma [37]. Nonetheless, quasi-stable fusion was first achieved by the soviet T-4 reactor in 1968 [36]. More recently, the flagship European reactor, the Joint European Torus (JET), recorded a record 16 MWt of fusion power, and achieved a net fusion energy release (Q) of 0.7 times the heating power required [38].

In 1986, an international collaboration was agreed between the Japan, the Soviet Union, United States and the European Union to create an international fusion facility that would eventually become the Iter reactor, which is currently under construction in France [39]. This reactor is planned to achieve sustained fusion with $Q = 10$ and produce 500 MWt of fusion power. This will be achieved using a much larger plasma volume and stronger magnetic fields than JET, resulting in a longer energy confinement time and maximum achievable pressure. First plasma is planned to be achieved in Iter in 2025, followed by the first D-T fusion in 2035 [40].

Iter will be followed by the DEMOnstration power reactor (DEMO), which is intended as a demonstration nuclear fusion power reactor [40]. This reactor is planned to have comparable electrical power output to a conventional fission reactor, and to begin operation between 2040 and 2050. A comparison of the JET, Iter and DEMO reactors is shown in table 1.1.
### 1.5 Components of Fusion

Aside from proving the immediate feasibility of achieving sustained ignition, there are many other engineering challenges that must be overcome to make fusion a viable power source. The work in this thesis is primarily to support and validate some materials choices for the Iter reactor currently under construction in France, and its planned successor, DEMO. As such, the challenges pertinent to this work can be explored through analysis of the key components of the Iter reactor, as presented in figure 1.9.

From a materials perspective, the effects of high temperature, impingement of plasma on the reactor wall and radiation damage from high energy (14.1 MeV) fusion neutrons are of key concern, as these effects may severely limit the lifetime of materials in the reactor. This has the potential to significantly increase the cost and maintenance requirements of a reactor, thus making fusion power uneconomical [15].

The main components that are exposed to these conditions are the first wall, blanket and divertor, as well as the structures that support them. The functions of these components, particular materials challenges and potential materials choices are explored in the following sections.

<table>
<thead>
<tr>
<th></th>
<th>JET [38]</th>
<th>Iter [40]</th>
<th>DEMO [41]</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Plasma</td>
<td>1983</td>
<td>2025*</td>
<td>2040*</td>
</tr>
<tr>
<td>Volume (m³)</td>
<td>90</td>
<td>840</td>
<td>2900*</td>
</tr>
<tr>
<td>Burn time (s)</td>
<td>-</td>
<td>1000</td>
<td>continuous</td>
</tr>
<tr>
<td>Q</td>
<td>0.67</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Maximum fusion power (MWt)</td>
<td>16</td>
<td>500</td>
<td>5000</td>
</tr>
<tr>
<td>Cost (2014 Million USD)</td>
<td>438</td>
<td>13,000*</td>
<td>-</td>
</tr>
</tbody>
</table>

*These estimates are subject to frequent change
1.5. Components of Fusion

Figure 1.9: Schematic of the Iter reactor, with key components highlighted: Dark blue denotes the divertor, orange: the vacuum vessel, light blue: magnets, light green: the cryostat, red: the blanket. Modified from [42].

1.5.1 The First Wall

The first wall is the material which directly faces the plasma, the key function of which is to shield other components from the effects of plasma instabilities and prevent contamination of the plasma by reactor materials. Materials selection for the first wall is based on several rigorous and sometimes contradictory requirements. In addition to having good radiation tolerance, the material must have a low vapour pressure at operating temperature ($<1000 \text{ K for Iter [43]}$) and have low atomic number to minimise radiative losses from the plasma. This is necessary as instabilities in the plasma, particularly edge localised modes [37] (visualised in figure 1.10), erode material from the first wall, material which is then subsumed into the plasma. Energy loss from the plasma ($Q^*$) is dominated by bremsstrahlung radiation, which is directly proportional to the atomic number of the radiating material.
1.5. Components of Fusion

Figure 1.10: Edge localised modes in the MAST reactor. Bright spots are where the plasma impinges on the first wall and divertor materials, bright filaments are the result of localised edge modes. Image credit: Culham Centre for Fusion Energy.

The material of the first wall must also have adequate thermal conductivity and thermal stability to prevent fatigue failure due to thermal cycling. Ideally the material must also have no long lived activation products to prevent the generation of long term nuclear waste (this being a key advantage of fusion over fission) and not be so activated or retain significant quantities of tritium so as to greatly increase the difficulty of maintenance [44].

The two obvious materials choices that meet these criteria are carbon and beryllium, the only materials with very low atomic mass that have reasonable structural and thermal properties. Both of these choices were tested in the JET reactor, which initially used a carbon first wall before transitioning to beryllium to more closely mimic the planned environment of Iter [45]. It was found that installation of the beryllium first wall dramatically decreased the fuel retained in the wall and led to lower radiative
1.5. Components of Fusion

losses in the plasma [46].

In the long term, for devices such as DEMO, plasma disruptions and edge localised modes are likely to become less frequent due to improvements in plasma confinement [47]. As such the requirement for low atomic number will be relaxed somewhat, and it is envisaged that tungsten may be used due to its superior thermal, erosion and hydrogen/helium implantation properties [48].

1.5.2 The Divertor

As the fusion reaction progresses, helium “ash” from the reaction as well as impurities from the first wall accumulate in the fusion plasma, inhibiting further fusion reactions. As such, “ash” must be removed during reactor operation. This is achieved by leaving open magnetic field lines at the bottom of the target chamber, which allow some of the plasma to escape. The escaping plasma contains both “ash” and fuel, the tritium in which must be recycled if fusion is to be economical. The plasma travels along the open field lines until it encounters the tiles of the divertor, before being channelled through external pumps for recycling [41].

The key considerations for the materials of the divertor tiles are excellent temperature stability and high thermal conductivity due to the very high thermal flux at the plasma strike points. In addition, the material must be resistant to sputtering and remain stable when implanted with hydrogen isotopes, helium and material sputtered from the first wall [47, 50]. The recognised choice of material for this is tungsten, which has an exceptionally high melting point (3697 K [51]), reasonable thermal conductivity (1.75 Wcm$^{-1}$K$^{-1}$ [52]), low thermal expansion coefficient (4.5 × 10$^{-6}$ K$^{-1}$ [53]) and good resistance to erosion by the plasma.
1.5. Components of Fusion

1.5.3 Tritium Breeding Modules

One of the key engineering challenges of D-T fusion is to produce enough tritium to sustain the reaction. This is necessary as tritium has a half-life of 12.32 years [10], which means that it does not exist in nature in appreciable quantities and is difficult to transport. Issues with transport notwithstanding, the total world supply of tritium is 1.5 kg/yr with 18.5 kg stored [54], whereas a 3 GW power reactor is envisaged to require as much as 180 kg/year [55]. Thus, tritium must be produced in Tritium Breeding Modules (TBM’s) in a future power reactor. Tritium breeding is achieved by using energetic neutrons from the D-T reaction to fission lithium:

\[ ^{6}\text{Li} + n \rightarrow ^{4}\text{He} + ^{3}\text{T} \quad (1.13) \]

\[ ^{7}\text{Li} + n \rightarrow ^{4}\text{He} + ^{3}\text{T} + n \quad (1.14) \]

The former of these is expected to provide the bulk of the tritium, as the latter is endothermic and has a high neutron energy threshold. These reactions alone are not sufficient to replace tritium used in the fusion reaction as each D-T reaction produces one neutron, which in turn can only produce one tritium atom. Obviously some neu-
1.6. Materials of Interest

tronns will be captured by other materials in the reactor, thus an additional source of neutrons is required.

Sufficient neutron economy may be achieved through the introduction of a neutron multiplier such as beryllium, lead or bismuth, which undergo (n,2n+) reactions. This produces additional neutrons, and may be sufficient to replace the tritium used in the fusion reaction, providing the breeding module is properly configured [56]. From this standpoint, the relevant metric for TBM designs is the tritium breeding ratio (TBR) (i.e. the overall ratio of tritium used/tritium produced for an entire reactor outfitted with such modules). Theoretically, the TBR must be above 1, however in practice some tritium will decay or be lost in the tritium recycling system, thus a TBR greater than 1.43 is desirable [55]. In addition to breeding tritium, TBMs will also be used to remove heat from the reactor for power generation.

Several design concepts exist, with six slated for testing in the Iter program. All are based on two core tritium breeding materials mixtures; the Li$_2$SiO$_4$-Be pebble bed and Li-Pb eutectic blankets, although in the long term liquid FLiBe ((LiF)$_2$BeF$_2$) concepts have also been proposed. An overview of the technological readiness, key requirements for further research, limitations and advantages of these designs is outlined in table 1.2.

1.6 Materials of Interest

Having examined the overall design and key components of the Iter and DEMO reactors, the materials proposed for use in these components, and which are the focus of
Table 1.2: Comparison of tritium breeding module concepts. Technological readiness assessments from [57]. TSP stands for “technological simplicity parameter”, which is an assessment of how many of the technical issues are already solved, DAP is the “DEMO attractiveness parameter”, and AAP the “advanced reactor attractiveness parameter”, an assessment of the technologies ultimate potential.

<table>
<thead>
<tr>
<th>TSP</th>
<th>DAP</th>
<th>AAP</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic breeder (steel structures)</td>
<td>high</td>
<td>high</td>
<td>med.-</td>
</tr>
<tr>
<td>Ceramic breeder (SiC structures)</td>
<td>low</td>
<td>very</td>
<td>high</td>
</tr>
<tr>
<td>Dual coolant (steel structures)</td>
<td>med.-</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>Self-cooled PbLi (SiC structures)</td>
<td>low</td>
<td>very</td>
<td>very</td>
</tr>
<tr>
<td>Flibe</td>
<td>med.</td>
<td>med.</td>
<td>med.-</td>
</tr>
<tr>
<td>Helium</td>
<td>very</td>
<td>very</td>
<td>very</td>
</tr>
</tbody>
</table>

the work presented in this thesis, are examined. In this section, only an overview of the basic properties of the materials are given, with more details relevant to the details of the simulations reported in this thesis, outlined in chapters 3-6.

### 1.6.1 Beryllium

Beryllium is a metal with low atomic mass (9.012 amu [10]), very low density (1.85 g/cm³ [58]) and high stiffness (287 GPa [59]). It occurs relatively rarely within the
earth’s crust and forms ores of Bertrandite \((\text{Be}_4\text{Si}_2\text{O}_7\text{(OH)})_2\) and Beryl \((\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18})\), with a total recoverable reserve using current commercial technology in excess of 400,000 tonnes \[60\]. Extraction from the ore is difficult owing to beryllium’s high affinity for oxygen, and is only carried out on an industrial scale in China, the US and Kazakhstan \[60\]. Machining and working with pure beryllium is also difficult as when inhaled, its dust can cause a significant allergic reaction known as berylliosis, even in concentrations as low as 0.1 \(\mu\text{gm}^{-3}\) of beryllium during chronic exposure \[61\]. Thus strict safety precautions must be in place when handling beryllium metal.

Due to its low natural abundance and difficulty in handling, it is expensive (510 USD/kg \[62\]) and thus used for relatively few niche applications where its unique physical, chemical and nuclear properties are required. In particular, its exceptionally low density, high stiffness and (relatively) high melting temperature are extremely attractive for aerospace applications where it has been used as structural components in rockets, missiles, planes and satellites as well as for precision instrumentation owing to its low thermal expansion coefficient \[63\]. In addition, due to its low atomic number it has a low interaction cross-section for high energy photons and charged particles making it ideal for use as a radiation window in X-ray machines and particle detectors \[63\].

Another consequence of its low atomic mass is that it is an effective moderator, and in the fission regime \((n < 2\text{MeV})\) has a low cross-section for inelastic interactions \[64\]. As such, Be and BeO have been used as neutron moderators and reflectors in several fission reactors, in particular where compactness is important such as in some submarine reactors, and more exotically, proposed nuclear rockets \[65, 66, 67\]. Beryllium is also utilised to produce neutrons through an \((\alpha,n)\) reaction which \(^9\text{Be}\) (which comprises 99% of natural Be) undergoes when bombarded with alpha particles. For fusion applications, it is utilised as a neutron multiplier as \(^9\text{Be}\) undergoes a \((n,2n)\) reaction
when bombarded with energetic neutrons [64]:

\[
\frac{9}{4}\text{Be} + \text{n} \rightarrow 2\frac{1}{2}\text{He} + 2\text{n}
\] (1.15)

At room temperature beryllium has a hexagonal close packed crystal structure (see figure 1.12) with an \( a \) parameter of 2.62 Å and \( c/a \) ratio of 1.568, 2\% below the ideal, indicating some degree of directional bonding and which causes strongly anisotropic thermal and mechanical properties [58]. The equilibrium nearest neighbour bond length is 2.26 Å, and second nearest neighbour 2.286 Å. The HCP crystal structure has 3 independent slip systems, two of which are easy: basal \( \{0002\}\langle11\bar{2}0\rangle \) with two slip modes and prismatic type-I planes \( \{10\bar{1}0\}\langle11\bar{2}0\rangle \) with two slip modes as well as pyramidal slip which is thermally activated. For effective ductility, at least six independent slip modes are required, thus beryllium is brittle at low temperatures and undergoes a brittle-ductile transition around 150° C, although this is heavily dependent on grain size [68, 69]. Within the HCP crystal structure there are six symmetrically distinct interstitial sites as outlined in figure 1.12b.

![Figure 1.12: Beryllium hexagonal close packed crystal structure with a) slip systems and b) interstitial sites marked. Structure from [58].](image)

From the perspective of fusion applications as a first wall and neutron multiplying ma-
1.6. Materials of Interest

terial in the TBM, there are three key concerns that may potentially limit its use. The first is the tendency of hydrogen and helium, implanted or radiogenic, to segregate to form large bubbles at fusion relevant temperatures [70, 71]. This leads to significant embrittlement of beryllium and increases the tritium inventory of the breeder module, making tritium recovery and maintenance difficult. The second is the general embrittling effect: increasing the brittle-ductile transition temperature due to irradiation, which, combined with void swelling leads to the formation of a fine powder which is a particular hazard due to the potential for berylliosis when inhaled. Finally, for first wall applications the resistance to thermal stresses and erosion caused by plasma transient impingement is a key concern [72, 43].

These issues have been addressed extensively from an experimental perspective, however it is presently not possible to fully replicate the fusion environment for the predicted lifetime of these components [45, 73, 72]. As such, a mechanistic understanding of radiation damage in beryllium is being pursued, underpinned by modelling efforts [74, 75]. To this end, the intrinsic defect chemistry of beryllium has been modelled systematically using Density Functional Theory (DFT) by Middleburg et al. [76]. Further, the extrinsic defect behaviour of several common impurities, and where relevant their segregation to secondary phases has also been investigated [77, 76, 78]. As mentioned previously, the accommodation and migration of hydrogen and helium is of particular interest, and has thus been extensively studied [79, 80]. These results will be discussed in more detail in chapter 3.

While defect behaviour at equilibrium is well understood, defect formation during radiation damage is less so (although some studies of damage cascades do exist [81]). As such, the work in this thesis focuses on simulating and characterising radiation damage processes in beryllium.
1.6.2 Beryllium Intermetallics

Beryllium rich intermetallics, in particular the $\text{Be}_{12}M$ series (where $M$ is a transition metal) have been proposed to replace pure beryllium in fusion applications. They potentially offer significant improvements in thermal stability, radiation tolerance, tritium retention and other thermo-physical properties while maintaining similar neutronic properties due to the large proportion of beryllium in the structure [56, 82]. To maintain sufficient neutronic properties, the alloying element must have a low neutron capture cross-section in the high and intermediate energy spectrum. Some of the systems identified for further investigation are Be-Ti, Be-V, Be-Mo and Be-W [56], the beryllium rich portion of the relevant phase diagrams are presented in figure 1.13

![Figure 1.13: Beryllium rich sections of the Be-Ti, Be-V, Be-Mo and Be-W phase diagrams reproduced from [83], [84], [85] and [86] respectively. Non-stochiometry of intermetallic compounds is, for the most part, poorly characterised and is not presented here.](image)
From a neutronic perspective, the chief beryllium replacement candidates are Be\textsubscript{22}M and Be\textsubscript{12}M as they have the composition most similar to pure beryllium. From a thermal stability perspective, Be\textsubscript{12}M has a much higher melting temperature and is therefore more attractive. Preliminary neutronic evaluations of Be\textsubscript{12}M substituted beryllium breeder blankets revealed that Be\textsubscript{12}Mo and Be\textsubscript{12}W do not have sufficient neutronic properties (i.e. a TBM designed with these materials would have too low a breeding ratio), however this does not preclude their use as first wall materials [56]. Further, the Be-W system is of interest as during operation of Iter, erosion of the beryllium first wall followed by transport and finally redeposition in the tungsten divertor are anticipated. Several studies have shown that Be-W intermetallics are likely to form, including Be\textsubscript{12}W [87]. For these reasons, the work in this thesis focuses on Be\textsubscript{12}M materials.

The Be\textsubscript{12}M series have a tetragonal crystal structure [88], first identified for Be\textsubscript{12}Fe and presented in figure 1.14. There is some controversy as to the structure of Be\textsubscript{12}Ti, as it has also variously been reported as being hexagonal. This is addressed in detail in chapter 3. The tetragonal I\textsubscript{4}/mmm structure consists of one transition metal site at (0,0,0) and three beryllium sites. The transition metal site is coordinated entirely by beryllium sites, whereas the beryllium sites are coordinated by a combination of other beryllium sites and transition metal sites [88].

Unlike beryllium, which has a long and rich history of use in the nuclear industry, Be\textsubscript{12}M compounds were only proposed as alternatives in the early 1990’s and have no uses outside fusion applications. As such there is relatively little data regarding their irradiation behaviour. Be\textsubscript{12}Ti and to a lesser extent Be\textsubscript{12}V have been better characterised than other materials in this series as they have been identified as more suitable for fusion applications [90, 91, 82]. Early results have been encouraging, with various irradiation studies showing Be\textsubscript{12}Ti to exhibit lower swelling, less degradation of ther-
1.6. Materials of Interest

Figure 1.14: Tetragonal crystal Structure of $\text{Be}_{12}\text{Ti}$ viewed in the [001] direction. The coordination of each site is highlighted with polyhedra (right). Structure from [89].

mal conductivity and mechanical properties, and all round better survivability than pure beryllium in thermal and fast neutron irradiation experiments [92, 93]. Further, both irradiation and ion implantation show lower hydrogen and helium retention than beryllium, as well as release at lower temperatures; potentially offering a significant advantage in terms of tritium inventory [91, 94].

While some efforts have been made to develop a mechanistic understanding of radiation damage in these systems, surprisingly little simulation work has been carried out, with the exception of a few DFT studies investigating the basic materials properties of $\text{Be}_{12}\text{Ti}$ [95] and more recently, the work of Allouche et al. who investigated the solution of hydrogen in $\text{Be}_{12}\text{W}$ [96]. Thus, significant work remains to be done.
1.6.3 Tungsten

Tungsten is a refractory metal with the highest melting temperature (3422°C) and lowest vapour pressure (above 1650°C) of any metal, low thermal expansion coefficient (4.5 $\mu$m$^{-1}$K$^{-1}$) and high thermal conductivity (173 WK$^{-1}$m$^{-1}$) [97]. Further it has extremely high density (19.25 gcm$^{-3}$) owing to its high atomic mass (183.84) and moderate bond length [97]. Tungsten is mined commercially in several countries, resulting in a moderate price (28.5 USD/kg) which is subject to fluctuation. Most tungsten produced is converted into tungsten carbide (discussed in section 1.6.4), however pure tungsten and tungsten alloys also have applications owing to their high melting temperature and good thermal stability. Due to its high density it is commonly used in munitions, particularly as the payload of kinetic energy penetrators. It is also a component in some superalloys such as hastelloy which are used in turbine blades, rocket nozzles and some nuclear reactors. These properties also make tungsten the best candidate material for the divertor of fusion reactors, and a candidate material for the first wall [48, 47].

Tungsten exhibits a BCC crystal structure, as shown in figure 1.15. The BCC crystal structure has no truly close packed planes, with the $\{110\}$ family being pseudo-close packed, and only 8 close packed directions $\langle 111 \rangle$. As such, its only slip system is thermally activated, meaning that it is brittle at low temperatures.

The use of tungsten in fusion reactors must take into account its neutronic properties. Natural tungsten is composed of five isotopes: $^{180}\text{W}$, $^{182}\text{W}$, $^{183}\text{W}$, $^{184}\text{W}$ and $^{186}\text{W}$, which have modest capture cross-sections for fast neutrons and undergo transmutation to form osmium, tantalum and rhenium through capture followed by beta decay [10]. This causes significant activation, with some concerns that the high residual radiation on shutdown may make maintenance difficult [98].
1.6. Materials of Interest

The irradiation properties of tungsten have been studied extensively via experimental techniques and simulated damage cascades, while its interaction with hydrogen, helium and beryllium have also been investigated experimentally and through the application of DFT [99, 99].

1.6.4 Tungsten Carbide

Tungsten carbide is an exceptionally hard material, the principal use of which is as coatings for cutting tools. Like pure tungsten, it also has high density (15.63 gcm\(^{-3}\)) so is commonly used in armour piercing munitions [100]. In addition, it has excellent thermal stability, with a melting temperature of 2870\(^\circ\)C, thermal expansion coefficient of 110 Wm\(^{-1}\)K\(^{-1}\), and a high thermal conductivity of (110WK\(^{-1}\)m\(^{-1}\)) [100].
1.6. Materials of Interest

Tungsten carbide has a hexagonal crystal structure (see figure 1.16), where tungsten and carbon form alternating pseudo-close packed layers on the \{0001\} planes. Alternately, this can be thought of as a simple hexagonal (i.e. not close packed) tungsten sublattice with carbon interstitials at alternate trigonal sites as direct carbon-carbon interactions are minimal.

Figure 1.16: Two full unit cells of the tungsten carbide crystal structure. Structure from [101].

Tungsten carbide has been used as a neutron moderator and reflector in early nuclear applications for assessing the criticality of weapon cores in the Manhattan project. It was used for this application specifically as while the carbon in tungsten carbide is an effective moderator (and by extension reflector), tungsten is an effective gamma shield. More recently, tungsten carbide is being considered for use as a radiation shield for neutrons (when combined with a neutron absorber). Given its similar thermal properties to pure tungsten, it is also being considered as a divertor material.
1.7 Modelling Radiation Damage in Materials

The primary motivation for work presented in this thesis is to contribute to predicting the behaviour of materials in a nuclear fusion environment over their lifetime. This section describes the basic theory of radiation damage in materials, and how materials modelling can be used to aid in understanding these processes. Particular focus is placed on contextualising the results of Density Functional Theory (DFT) and Molecular Dynamic (MD) simulations, the two principal techniques used in this thesis.

As demonstrated in section 1.5, the nuclear fusion environment is an incredibly challenging environment for materials survivability, with high fluxes of fusion neutrons, high thermal flux, thermal transients and high temperatures. This environment is difficult and expensive to replicate, and currently cannot be completely replicated as no sufficiently high flux source of fusion neutrons exists. As such, materials behaviour over the lifetime of the reactor must be extrapolated from limited and incomplete experimental data.

It is only possible to predict the behaviour of fusion materials with some degree of reliability if a mechanistic understanding of the materials evolution under fusion conditions is achieved; otherwise it is possible that hitherto unknown processes may cause drastic divergence from extrapolated data [102]. This is where computational modelling is useful, as it may be used to probe and simulate conditions, time scales and length scales that cannot be accessed experimentally. That is, combined with experimental data, a more complete picture of the materials behaviour may be constructed.
1.7. Modelling Radiation Damage in Materials

1.7.1 Theory of Radiation Damage

Interaction of Radiation with Matter: Defect Formation

In both fission and fusion reactors, the highest flux of radiation and principal cause of radiation damage is that from neutrons. Energetic neutrons in the MeV range interact with nuclei in the material either elastically, in which the total momentum of the incident neutron and nucleus is conserved, or inelastically where it is not. During inelastic interactions, the incident neutron may either excite the internal structure of the nucleus or be captured, transmuting the atom. Both processes are strongly element dependent, and unless functionally necessary as in a neutron multiplier, are selected against when choosing materials to avoid unwanted transmutation products and residual radiation. Thus, in most structural materials used in reactors, the elastic interaction cross-section is orders of magnitude higher than the inelastic cross-section. It is, however, still low in absolute terms, hence neutrons can penetrate far into a material [103].

When an energetic neutron interacts with a nucleus elastically, it transfers kinetic energy to that nucleus inversely proportional to the nucleus’ mass [104]. At sufficiently high energy, this displaces the nucleus which may then itself be considered a form of charged radiation (depending on the energy and material) referred to as a Primary Knock-on Atom (PKA). As charged radiation, the PKA undergoes ballistic collisions with other nuclei in the material generating other knock-on atoms thus causing a damage cascade, but it also interacts electronically with the electrons in the material. These interactions are summarised in figure 1.17.

Both these modes of interaction can cause defects, with electronic interactions causing
1.7. Modelling Radiation Damage in Materials

Electronic stopping dominates
Nuclear stopping dominates

Figure 1.17: Typical trajectory of energetic neutron and scattered ions in a material.

electronic defects, such as charge defects:

\[ A_A^x + B_B^x \rightarrow A_A' + B_B \]  \hspace{1cm} (1.16)

Nuclear interactions may result in further atomic displacements creating Frenkel pairs, denoted for pure beryllium as

\[ \text{Be}_{\text{Be}} \rightarrow V_{\text{Be}} + \text{Be}_i \]  \hspace{1cm} (1.17)

In metals (which are the focus of this thesis), electronic defects are typically insignificant as they rapidly recombine [15]. Frenkel pairs, however, form the basis of many deleterious effects of radiation in materials and thus merit further consideration.

Several models aim to describe the number of Frenkel pairs or displacements produced by a PKA as a function of energy, E. The original of these is the Kinchin-Pease (KP) model [105], which was later modified to the Norgett-Robinson-Torrens (NRT) [106] and Greenwood models [107]. These are presented in figure 1.18. There are two key metrics in the Kinchin-Pease model; the energy at which nuclear stopping becomes
1.7. Modelling Radiation Damage in Materials

dominant over electronic stopping, $E_c$; and the threshold displacement energy, $E_d$. The latter is defined as the lowest primary knock-on energy $E$ at which a displacement may occur. In all models, no displacements occur below $E_d$ and between $E_d$ and $2E_d$ one displacement occurs, except for in the Greenwood model. Above this energy the models differ. For the KP model, each additional two increments in $E_d$ give rise to another displacement until $E_c$ is reached, where electronic stopping dominates. In the NRT model, the gradient of this intermediate regime is modified by a constant, $k$, which is fitted to experimental data (see fig 1.18). In the Greenwood model, $k$ is a variable and depends on $E$, which again is fitted to experimental data. All three models include the transition to electronic stopping, thus are capable of describing energies at which electronic stopping dominates. These models are referenced with respect to beryllium, carbon, tungsten and tungsten carbide in chapter 4.

![Graphical illustrations of the Kinchin-Pease, NRT and Greenwood displacement models. Equations given right.](image)

Figure 1.18: Graphical illustrations of the Kinchin-Pease, NRT and Greenwood displacement models. Equations given right.
Evolution of Defects: rate theory

The relative ease of formation of point defects due to radiation damage is only one contribution to the radiation response of material. Intuitively, materials with a higher $E_d$ (i.e. those in which it is harder to form radiation induced defects) should be more radiation tolerant than those with low $E_d$. This is not necessarily the case, as a higher $E_d$ is strongly correlated with a higher defect energy, meaning that for each defect more energy is stored in the material. If enough energy is stored in the material, a more disordered phase may become favourable and the material may become amorphous.

A further, and perhaps the dominant consideration, is how the defects behave in the material. Defects interact via long range elastic interactions. Depending on the nature of these interactions, defects can either recombine and annihilate, in which case the material will likely have good radiation tolerance, or they can segregate together to form clusters and then extended defects such as dislocation loops, voids and precipitates. This is complicated further when common transmutation products are considered, in particular hydrogen and helium which can stabilise small defect cluster and cause bubble formation.

The formation of extended defects from point defects depends on thermodynamics (i.e. whether it is energetically favourable) and kinetics (i.e. the rate at which these defects can form). The former may be quantified by the relative Gibbs free energy ($G$) of a point defect ($D_{iso}$) and an extended defect ($D_{ext}$) separately and the combined extended and point defect (i.e. longer extended defect)

$$\Delta G = G(D_{ext}) + G(D_{iso}) - G(D_{ext}D_{iso})$$  (1.18)
It should be noted that for the addition of a point defect to an extended defect, this is likely to be a function of the size of the defect, particularly when the extended defect is small, meaning that nucleation effects may be significant. The kinetics of extended defect formation are influenced by the elastic interactions of extended and point defects, but is principally dictated by the diffusivity of the point defects. The diffusion coefficient can be approximated using equation 1.19,

\[ D = D_0 \exp \left( \frac{E_a}{k_B T} \right) \]  

(1.19)

where \( E_a \) is the activation energy and \( D_0 \) is the maximal diffusion coefficient. For a thermal equilibrium concentration of defects, \( E_a \) is composed of two terms, the defect formation energy and the lattice hop energy, \( E_{\text{hop}} \). Radiation damage creates a defect concentration far above equilibrium, so \( E_a \) can be approximated as \( E_{\text{hop}} \). Equations 1.18 and 1.19 must be considered for each possible defect reaction and migrating species respectively. Further, both \( \Delta G \) and \( D \) are temperature dependant and as a result the behaviour of a material can shift dramatically with temperature. Thus, extrapolation of trends across temperature can only be achieved with confidence if the underlying mechanisms driving these trends are well understood.

**Evolution of macroscopic properties**

The evolution of extended defects has consequences for the macroscopic properties of materials. In metals, two effects which usually limit the lifetime of a component are radiation induced embrittlement and swelling [15]. Embrittlement occurs when the dramatically increased concentration of defects pins dislocations within the material, and the dislocations themselves become entangled. This prevents movement of dislocations, which is necessary for plastic deformation, causing the yield strength of the material to increase to the ultimate tensile strength, resulting in brittle behaviour [15].
1.7. Modelling Radiation Damage in Materials

Swelling occurs when vacancies coalesce to form voids, increasing the void fraction of the material and thus the macroscopic dimensions. This is heavily temperature dependent [15], with low diffusion limiting void formation at low temperatures, and thermal emission limiting it at high temperatures. Thus, metals typically undergo swelling in the temperature range $0.3 \, T_m < T < 0.55 \, T_m$ [15], where $T_m$ is the melting point of the material.

Transmutation may compound the effect of void swelling, particularly where hydrogen and helium are evolved as they segregate to vacancies and vacancy clusters, eventually forming bubbles. Further, a wide range of transmutation products may occur leading the formation of secondary phases and precipitates. Many of these effects are lifetime limiting for components in both fission and fusion reactors. As such, it is vital that a mechanistic understanding of these processes is developed.

1.7.2 Multiscale Modelling

Given the complex process occurring on an atomistic scale that dictate the evolution of materials properties during irradiation, simulation can be a valuable tool to develop our understanding of radiation damage in materials. In the past 50 years, a rapid increase in computational capacity has opened several fields of modelling for this purpose. Each of these fields is limited in the length scales and timescales that can be simulated, but together can access a broad range, as outlined in figure 1.19. Typically, the longer length and time scales that can be simulated the more approximations must be introduced.

On the smallest length and time scales, ab-initio techniques are used to simulate the electronic structure of tens to hundreds of atoms for hundreds of picoseconds. These
1.7. Modelling Radiation Damage in Materials

Figure 1.19: Length and timescales typically accessible using several common modelling methods.

can be used to calculate point defect properties such as formation energy and hopping energies familiar from equations 1.18 and 1.19. In this thesis, such simulations are performed using DFT, the details of which are explored in chapter 2, section 2.1.

Beyond this, MD simulations (see chapter 2 section 2.4) can access up to $10^9$ atoms and ns timescales. This allows the simulation of phenomena unavailable to DFT, such as damage cascades and extended defects. Further, it can be used to identify complex processes such as concerted migration, that are not accessible in static simulations with few atoms [108]. MD simulations rely on empirical potentials, the form of which approximate the physics of the real system, and which contain constants (parameters) that must be fitted to experimental data. Where no such data exists, DFT data may suffice. More often, properties predicted using empirical potentials are compared to those predicted using DFT, which is more universally applicable and the limitations of which are well understood, thereby providing useful validation.
The MD approach can be extended to longer timescales using Accelerated Molecular Dynamics (AMD), which uses statistical mechanics to accelerate the rate of infrequent events predicted by MD [15]. This approach similarly relies on the empirical potential form, though further approximations and assumptions are introduced to achieve the acceleration [15].

Even greater length and timescales can be accessed using kinetic Monte-Carlo methods. In these methods, a known initial state is allowed to evolve over time through some transition event that has a known probability of occurring [109]. A uniform random number is generated to decide whether the transition occurs, and then the process is repeated. Such approaches do not explicitly model each atom in the material unlike MD and DFT, rather they only model the phenomenon of interest explicitly (e.g. dislocations). A typical example of such a method is the simulation of defect mobility and clustering [109]. Again, defect diffusivity and thermodynamic data is necessary for such a simulation, and can be provided either from the results of DFT and MD simulations or from experimental data.

Another example of an accelerating method is the binary collision approximation, which forms the basis of the popular SRIM software [110]. This method can be used to calculate the final distribution of incident energetic ions in a material, along with the distribution of atomic displacements and much other useful information. To calculate the number of displacements, the code requires input of the threshold displacement energy of the elemental species that make up the material, which can be determined experimentally or through MD simulations [15].

Even longer time and length scales can be accessed using continuum modelling ap-
proaches such as finite element analysis. These approaches model the material (or elements of it) as a continuum, the properties of which must be defined. These properties can be linked to the microstructural evolution of the material as outlined in section 1.7.1. As such, properties that can be predicted using information about the microstructure from KMC simulations may be used in such models in lieu of experimental data where none is available.

1.8 Structure of this Thesis

Having outlined the components and requirements of nuclear fusion reactor components and the materials considered for these applications, it is clear that additional work is required to understand how such materials will evolve in a reactor. The techniques used to address this challenge are outlined in the following methodology chapter. The structure of Be$_{12}$Ti and results of elastic neutron scattering experiments across the Be$_{12}M$ materials series are presented in chapter 3. The properties and migration of intrinsic defects in the Be$_{12}M$ series are investigated in chapter 4. Threshold displacement damage profiles in the fusion reactor materials beryllium, tungsten, carbon and tungsten carbide are investigated in chapter 5. Finally, ongoing work and areas that require further investigation are outlined in chapter 6.
Chapter 2

Methodology

This chapter outlines the techniques employed in the simulations used throughout this thesis. Particular focus is placed on the limitations and accuracy of these techniques so that the results can be better contextualised.

Atomistic simulation requires two principal elements: a physical description of the atomic configuration and a model by which to evaluate the energy landscape of the atomic system. As the materials investigated in this thesis are all crystalline solids, a description of the atomic configuration can be provided by a basis and a motif, that is, a cell vector and a periodic repeating arrangement of atoms at each point. To make atomistic simulation possible on such a system, several approximations must be made regarding this description, which are outlined in sections 2.2 and 2.4.

The energy of the system for a static 3D arrangement of atoms can be described in several ways, resulting from different approximations of the physics in the real system. Two such descriptions are used in this thesis, quantum mechanical methods based on a (partial) solution of the Schrödinger equation, and empirical methods that use
functional forms to approximate various physical effects. Both these approaches have advantages and disadvantages, outlined in chapters 2.1 and 2.3.

2.1 Density Functional Theory

Quantum Mechanical (QM) approaches to describing an atomic system have the advantage that they are constructed from first principles, and thus in their purest form, are not compromised by empirically derived constants. In practice, many approximations and assumptions must be introduced to make these approaches tractable for all but the simplest systems. This section provides an overview of the theory underlying Density Functional Theory (DFT), with focus on the assumptions and approximations required to make it a practical simulation technique.

All QM approaches are based fundamentally on finding a solution to the Schrödinger equation,

\[ E\Psi = H\Psi \]  \hspace{1cm} (2.1)

where \( E \) is the total energy of the system, \( H \) is the Hamiltonian operator and \( \Psi \) is a set of solutions, or eigenstates, of the Hamiltonian. In the case of atomic systems, these eigenstates correspond to individual electron wavefunctions. The definition of the Hamiltonian depends on the physical system being described, and in the case of an atomic system can be split into five constituent contributions;

\[
E\Psi = \left[ -\frac{\hbar^2}{2m_i} \sum_{i=1}^{i=n} \frac{\nabla^2_{r_i}}{r_i} - \frac{\hbar^2}{2M_i} \sum_{i=1}^{i=n} \frac{\nabla^2_{R_i}}{R_i} + \sum_{i=1}^{i=n} \frac{e^2}{2|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{i=n} \frac{e^2}{2|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi 
\]  \hspace{1cm} (2.2)
where $T_n$ is the kinetic energy of electrons ($n$), $T_N$ the kinetic energy of nuclei ($N$), $U_{nn}$ the interactions of electrons with each other, $U_{NN}$ the interactions of nuclei with other nuclei and $U_{nN}$ the interaction of nuclei with electrons. $\Phi$ is a many body problem which has $4n$ dimensions (3 dimensions + spin for each electron, $n$) which is prohibitively computational expensive to solve, thus several approximations must be included. The first of these is the Born-Oppenheimer approximation [111], which states that given the large discrepancy in mass between electrons and nuclei they may be treated separately. Thus, $U_{NN}$ and $T_N$ are evaluated separately through classical means, and the Schrödinger equation, with the now simplified Hamiltonian, is evaluated for a stationary arrangement of nuclei in space. Further, the term for electron-nuclei interactions, which are coulombic, can be treated as an external potential, $V_{\text{ext}}$. Therefore $H$ is simplified to $H = -T_n + U_{nn} + V_{\text{ext}}$.

In effect, solving the Schrödinger equation for this reduced Hamiltonian defines the electronic orbitals, which allows the total forces on each atom resulting from the electronic system to be evaluated. As a consequence, simulation techniques outlined in sections 2.2 and 2.4 can be used to calculate various properties of the system.

### 2.1.1 Hohenberg, Kohn and Sham

Although greatly reduced in complexity, solving the reduced Schrödinger equation is still non-trivial. The electronic wavefunction, $\Psi$, is a function for every spatial coordinate of each of the $n$ electrons ($\Psi = \Psi(r_1, ..., r_n)$), which using the Hartree approximation [112], can be described as a product of individual electron wavefunctions ($\Psi = \Psi_1(r), ..., \Psi_n(r)$). This is a necessary step, as the full wavefunction for a simple molecule such as $O_2$ would be a 48-dimensional function (3 dimensions for each electron neglecting spin), which is impractical to solve.
It should be noted that the electron wave function cannot be measured experimentally. What can be measured however, is the probability of finding an electron in a given space at a given time; the electron density, \( n(r) \). The electron density can conveniently be calculated from the wavefunction by taking the conjugate of the function. For a generalised, ground state molecular system, in conjunction with the Hartree approximation, this gives:

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

(2.3)

where the factor of two appears because the Pauli exclusion principle states that each electron wavefunction can be occupied by two electrons if they have different spin.

The electron density gains additional significance considering the work by Kohn, Hohenberg and Sham [113, 114]. Kohn and Hohenberg proved two mathematical theorems that form the basis of DFT. The first states “The ground-state energy from Schrödinger’s equation is a unique functional of the electron density”. The significance of this, is that if the electron density, \( n(r) \), is known, the energy of the system can be found if the functional relating the two, \( E[n(r)] \), is also known. Unfortunately, this theorem says nothing as to the form of the functional.

The second Hohenberg-Kohn theorem states “The electron density that minimises the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation”. The practical implication of this is that if the true form of the functional is known, then the electron density could be varied to minimise the energy given by the functional, thus providing a means to find the relevant electron density. While the exact form the functional is not known, the general contributions
2.1. Density Functional Theory

can be surmised from the Hamiltonian as below:

\[ E[(\Psi_1)] = E_{\text{known}}[(\Psi_1)] + E_{\text{XC}}[(\Psi_1)] \]  

(2.4)

\[ E_{\text{known}}[(\Psi_1)] = -\frac{\hbar^2}{m} \sum_i \int \Psi_i^* \nabla^2 \Psi_i d^3r 
+ \int V(r)n(r)d^3r + \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|r - r'|} d^3r d^3r' \]  

(2.5)

Where the known terms consist of the electron kinetic energies, the external potential from the nuclei (Born-Oppenheimer approximation), the coulomb interactions between electrons, and between nuclei. The final and unknown term, \( E_{\text{XC}} \), by definition contains all the unknown quantities, but principally exchange and correlation effects.

This formulation, when combined with the Hartree approximation\[112\], leads to the Kohn-Sham equations for single electron wavefunctions \[113, 114\]:

\[ \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(r) + V_H(r) + V_{\text{XC}}(r)\right] \Psi_i(r) = \epsilon_i \Psi_i(r) \]  

(2.6)

\[ V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3r' \]  

(2.7)

Where \( V_{\text{ext}}(r) \) is familiar from equation 2.2, and \( V_H \) is the Hartree potential which describes the coulombic interactions between electrons (including an unphysical self interaction energy). The final term, \( V_{\text{XC}} \), is the exchange correlation potential, which is formally defined as the functional derivative of the exchange-correlation energy, but also must account for the unphysical interaction energy from \( V_H \).
2.1.2 Exchange-Correlation Functional

Using the Kohn-Sham equation, the electron density and energy of the system can be calculated iteratively from an initial, trial electron density. The only element that is missing is the form of the Exchange-Correlation functional, $V_{XC}$. The exact form of this functional is not known, however there is one case where it can be defined exactly: a uniform electron gas. This is not a particularly interesting case, as in a real system the variations in electron density are exactly what give rise to properties such as bonding. Fortunately (and perhaps surprisingly), it can be extended to real systems, by setting the exchange-correlation functional to the known value for a uniform electron gas with the local electron density observed at that position:

$$V_{XC}(r) = V_{\text{electrongas}}^{XC}[n(r)]$$  \hspace{1cm} (2.8)

This is known as the Local Density Approximation (LDA)\cite{113, 114}. The LDA is still widely used for DFT simulations to date, however it is important to remember that this does not represent an exact solution of the Schrödinger equation, and thus is not suitable for the simulation of some systems, particularly those in which there is a steep gradient in the electron density (e.g. where covalent bonds are present). As such, a wide variety of other functionals have been developed to improve on this approximation. The most widely used and simplest of these is the Generalised Gradient Approximation (GGA) \cite{115, 116, 117}. In the GGA scheme, the local gradient of the electron density is also incorporated into the functional:

$$V_{XC}^{\text{GGA}}(r) = V_{XC}[n(r), \nabla n(r)]$$  \hspace{1cm} (2.9)

There are many ways to incorporate this additional information and hence several variants of this scheme have been implemented, notably the Perdew-Wang functional
(PW91) and the Perdew-Burke-Ernzerhof (PBE) functionals. This approach is extended further in meta-GGA functionals, which take into account the second derivative of the electron density:

$$V_{XC}^{mGGA}(r) = V_{XC}[n(r), \nabla n(r), \nabla^2 n(r)]$$  \hspace{1cm} (2.10)

an example of which is the TaoPerdewStaroverovScuseria (TPSS) functional. In deciding which functional to use, it is important to consider the nature of the system as encoding more physical parameters of the system does not necessarily translate to an increase in accuracy. In particular, the LDA functional is typically more accurate for systems where the electron density tends to be more uniform, whereas GGA functionals are often more accurate for systems with steep changes in the electron density such as covalent and ionic materials.

The GGA-PBE functional has been selected for simulations in this work as it preserves the accuracy of the LDA for metallic systems while correcting (and sometimes overcorrecting) the LDA overbinding issue and discrepancy with experimentally derived binding energies. A comparison of predictions made using DFT in conjunction with the LDA, GGA-PW91 and GGA-PBE functionals and compared to experimental values is shown in table 2.1.

A further consideration is whether the functional contains empirically derived information. Such functionals, by design, work extremely well for systems similar to those they are fit to, however may become unphysical for dissimilar systems. All the functionals mentioned thus far are nonempirical.
Table 2.1: Comparison of lattice parameters predicted by the LDA, GGA-PBE and GGA-PW91 functionals with experimental values.

<table>
<thead>
<tr>
<th>Material</th>
<th>Par.</th>
<th>Exp.</th>
<th>LDA value</th>
<th>Δ %</th>
<th>GGA-PBE value</th>
<th>Δ %</th>
<th>GGA-PW91 value</th>
<th>Δ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>a (Å)</td>
<td>2.285 [122]</td>
<td>2.227</td>
<td>2.54</td>
<td>2.265</td>
<td>0.88</td>
<td>2.266</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>c/a</td>
<td>1.568 [122]</td>
<td>1.580</td>
<td>-0.77</td>
<td>1.576</td>
<td>-0.51</td>
<td>1.574</td>
<td>-0.38</td>
</tr>
<tr>
<td>Ti</td>
<td>a (Å)</td>
<td>2.951 [123]</td>
<td>2.865</td>
<td>2.91</td>
<td>2.939</td>
<td>0.41</td>
<td>2.933</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>c/a</td>
<td>1.587 [123]</td>
<td>1.582</td>
<td>0.32</td>
<td>1.583</td>
<td>0.25</td>
<td>1.582</td>
<td>0.32</td>
</tr>
<tr>
<td>V</td>
<td>a (Å)</td>
<td>3.026 [123]</td>
<td>2.926</td>
<td>3.30</td>
<td>2.994</td>
<td>1.06</td>
<td>2.990</td>
<td>1.19</td>
</tr>
<tr>
<td>Mo</td>
<td>a (Å)</td>
<td>3.146 [123]</td>
<td>3.113</td>
<td>1.05</td>
<td>3.161</td>
<td>-0.48</td>
<td>3.163</td>
<td>-0.54</td>
</tr>
<tr>
<td>W</td>
<td>a (Å)</td>
<td>3.165 [123]</td>
<td>3.137</td>
<td>0.88</td>
<td>3.184</td>
<td>-0.60</td>
<td>3.184</td>
<td>-0.60</td>
</tr>
<tr>
<td>Be_{12}Ti</td>
<td>a (Å)</td>
<td>7.35 [89]</td>
<td>7.250</td>
<td>1.36</td>
<td>7.361</td>
<td>-0.15</td>
<td>7.335</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>c/a</td>
<td>0.57 [89]</td>
<td>0.563</td>
<td>1.23</td>
<td>0.566</td>
<td>0.70</td>
<td>0.566</td>
<td>0.70</td>
</tr>
</tbody>
</table>

2.1.3 Spin Polarisation

As electrons are fermions, they can adopt one of two spin states. Conceptually, this adds a degree of freedom to the electron wavefunctions, in addition to the three spatial ones. As fermions, electrons must also obey the antisymmetric mixing rule for all fermions, which, in addition to giving rise to the Pauli exclusion principle is also the source of exchange. This is incorporated in the Hartree-Fock method [112] by using a Slater determinant, in which the N-electron wavefunction is expressed as the determinant of a matrix of single electron wavefunctions. For wavefunction with two electrons, j and k, the Slater determinant is:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \det \begin{vmatrix} \chi_j(x_1) & \chi_j(x_2) \\ \chi_k(x_1) & \chi_k(x_2) \end{vmatrix} \quad (2.11)$$

This ensures that a physical description of electron exchange is built in implicitly, in that when two electrons are exchanged it changes sign and it disappears if two electrons have the same wave function or occupy the same position, thus satisfying the Pauli exclusion principle. DFT uses an entirely analogous approach to the same effect.
2.1.4 Pseudopotentials

As has been demonstrated, using the Born-Oppenheimer and Hartree approximations in conjunction with the Kohn-Sham method, solution of the Schrödinger equation for complex systems is reduced to iteratively solving \( n \) three-dimensional functions, where \( n \) is the number of electrons. This, however, is still computationally demanding. The computational cost can be reduced further by employing the frozen core approximation [124]. The chemistry of any system is principally governed by the behaviour of the outer, valence electrons while the inner, core electrons do not participate in the formation of bonds. As such, although the core electrons cannot be neglected entirely, it can be assumed that only their effect on the outer valence electrons is significant. Thus, from a computational perspective, it is useful to approximate their effect on the outer electrons rather than treat them explicitly. This is achieved by the introduction of a pseudopotential to replace the electron density from the core electrons. The effect of this on the valence electrons is that of an external potential [124, 125]. One of the main implications is that the core electrons are effectively “frozen” and thus do not respond to changes in the electron density of the valence electrons. It is implicit in this approximation that these potentials are transferable from the elemental system to a compound, providing a suitable set of core electrons and cut-off radius, \( r_c \), of the pseudo-potential are identified [126, 127]. The cut-off radius is an essential parameter of the pseudopotential scheme, as beyond this cut-off, to ensure the exactness of the results, the pseudo-potential must overlap exactly with the electron density it is replacing (as shown in figure 2.1). \( r_c \) is element dependent, but is usually between 0.5-1.2 Å for most systems, although it may be significantly less for ultra-high pressure simulations [127].

Several pseudopotential schemes have been developed, of which three of the most widely used were considered for this work. The first are norm conserving pseudo-
Figure 2.1: Wavefunctions for titanium pseudopotentials (solid lines) overlayed against the all electron potential (dashed lines). The vertical line represents the cutoff radius, beyond which the pseudopotentials and all electron potentials are identical.
2.1. Density Functional Theory

potentials [128], which impose the additional constraint that the total charge of the pseudo-potential must be the same as the total norm of the all-electron potential. This simplifies numerical operations within DFT, and is a good physical representation of the system. It does however lead to the need for harder pseudo-potentials [127] ("harder" in this case refers to the need for a higher cutoff energy: see section 2.1.4), which increases the computational expense of simulations.

Second are the ultrasoft pseudopotentials (USPP) based on work by Vanderbilt [129]. These potentials remove the criteria that the total charge of the wavefunction is conserved, and consequently allow for significantly softer potentials, which by extension are much more computationally efficient. One of the drawbacks of this approach is that they contain at least one (and often many) empirical parameters, although for commonly used potentials these have been rigorously qualified [130].

The final approach is the Projector Augmented Wave (PAW) method [131, 132, 133], which combines the pseudo-potential approach with the linear augmented plane wave method to reintroduce near core oscillations of the valence electron wavefunctions. This is attractive as by comparison to USPPs it is a more physical representation and contains no empirical parameters, it is however more computationally expensive. Extensive comparison has been made between the USPP, PAW, norm conserving and all electron (no pseudo-potential) methods, which have shown excellent agreement in all cases except where atoms have very different electronegativities or strong magnetic moments [130, 134]. Considering this, USPPs were used in this work as none of the materials investigated fall into these categories.
Plane Waves

Even with the approximations outlined thus far, DFT is still computationally expensive by comparison to empirical potentials and simulations are usually limited to hundreds of atoms. This poses a challenge for the simulation of bulk properties, as for an isolated cluster of a few hundred atoms, surface terms will dominate, obscuring bulk effects. This necessitates the introduction of periodic boundaries, whereby an atom interacts across the boundary of the cell with its periodic image.

Given that DFT is concerned with evaluating electron wavefunctions, the introduction of periodic boundaries has the additional implication that the wavefunctions (and consequently any quantity derived from them) must also be periodic in space with the same periodicity as the (repeat unit) supercell. This is stated by Bloch’s theorem \[135\] for a wavefunction evaluated at a single \( \mathbf{k} \)-point:

\[
\psi_k(\mathbf{r}) = u(\mathbf{r}) e^{i \mathbf{k} \cdot \mathbf{r}} \tag{2.12}
\]

By extension, the overall wave function is given:

\[
\psi(\mathbf{r}) = \int \psi_k(\mathbf{r}) d^3\mathbf{k} \tag{2.13}
\]

and the electron density:

\[
\rho(\mathbf{r}) = \int |\psi_k(\mathbf{r})|^2 d^3\mathbf{k} \tag{2.14}
\]

where \( u_k \) is a function with the same periodicity as the unit cell and \( \mathbf{k} \) is a vector representing the position in reciprocal space. The functions \( e^{i \mathbf{k} \cdot \mathbf{r}} \), known as plane waves, are simply an arbitrary phase factor which scales the periodic function in surrounding cells. As such, it is only necessary to evaluate the integral of equation 2.12 over the
unit cell as defined in reciprocal space, also known as the Brillouin zone.

\(u(r)\) from equation 2.12 can be expanded in terms of a special set of plane waves:

\[
u_k = \sum G C_G e^{iG \cdot r} \quad (2.15)
\]

where \(G\) are wavevectors which satisfy the periodicity and symmetry of the crystal and \(C_G\) are Fourier coefficients. Equation 2.12 then becomes:

\[
\psi_k(r) = \sum_G C_{k+G} e^{i(k+G) \cdot r} \quad (2.16)
\]

To solve this for even a single point in \(k\)-space \(G\) must be summed over infinite possible values, which is obviously impossible. Fortunately, the physical meaning of solution at each \(G\) gives some insight into how it may be evaluated; each \(G\) represents a solution of the Schrödinger equation with kinetic energy given by:

\[
E = \frac{\hbar^2}{2m} |k + G|^2 \quad (2.17)
\]

Solutions with lower kinetic energy are more physically important than those at higher energy, thus some energy cutoff, \(G_{cut}\), may be employed, which reduces the infinite sum in equation 2.16 to the readily solvable

\[
\psi_k(r) = \sum_{|G+k|<G_{cut}} C_{k+G} e^{i(k+G) \cdot r} \quad (2.18)
\]

\(G_{cut}\) is chosen to balance convergence to an exact solution and computational efficiency, and further is element dependent. In this work, a convergence of at least \(10^{-3}\) eV atom\(^{-1}\) was employed (see figure 2.2), and the highest cutoff chosen for each element in a system used for the overall system. Where quantities are compared between systems (e.g.
2.1. Density Functional Theory

a compound and elemental system, as is necessary to calculate formation energies) the same cutoff is used for both systems to avoid the introduction of systematic errors.

A new form of the ultra-soft pseudo potentials is implemented in the most recent versions of CASTEP [136, 137](The DFT code used in this work) and was used for phonon calculations in this work, the convergence for which is shown in figure 2.2. Based on these convergence tests, a cut-off energy of 480 eV was used for defect energy calculations using Castep 6, while a cut-off of 660 eV was used for phonon calculations using Castep 8 and later.

Figure 2.2: Energy cutoff convergence for elements studied for Castep 6 and 8. Castep 8 was released part way through this work and includes modified pseudopotentials. Convergence criteria of $10^{-2}$ eV/atom is shown with a dotted black line. This is reached at 480 and 660 eV for all species in Castep 6 and 8 respectively.
k-points

Returning to equation 2.12, provided the function varies slowly over k-space, it is sufficient to evaluate it at a discrete series of k-points with in the Brillouin zone, and using linear interpolation to approximate the integral. Typically, however, other methods of interpolation such as Legendre Quadrature Methods provide a much faster convergence with respect to the number of k-points so this approach is used instead [130].

The number and arrangement of k-points also has a significant impact on the accuracy of the integral, as well as on the computational cost of evaluating it. The scheme developed by Monkhorst and Pack [138] is the most widely used method of choosing k-points, which defines a linear array within the Brillouin zone. The number of k-points can further be reduced when symmetry is considered, as equation 2.12 then only needs to be evaluated over the irreducible Brillouin zone (IBZ). Convergence with the number of k-points used, with uniform spacing based on the Monkhorst and Pack scheme is shown in figure 2.3. Based on this convergence test, a grid of $4 \times 4 \times 8$ k-points (from which 12 are used) was selected for the Be$_{12}$M structure, corresponding to a k-point spacing of $0.02 \ \text{Å}^{-1}$ which was then used for calculations of other structures. A more dense k-point grid of $8 \times 8 \times 14$, corresponding to a spacing of $0.012 \ \text{Å}^{-1}$ was used for phonon calculations which are more sensitive to small changes in the force field and thus require a higher k-point density. An even number of k-points was chosen for the Be$_{12}$M structure so that $2 \times 2 \times 2$ supercells could be investigated with exactly the same k-point spacing.
2.1.5 A note on Metals

One of the basic premises of the validity of the plane wave approach is that function 2.12, varies slowly over \( \mathbf{k} \) space. This is not the case for metals, where regions of space unoccupied by electrons are separated from occupied regions by the Fermi-surface. As such, the function changes discontinuously from zero to non-zero values, and thus would require an impractically dense grid of \( \mathbf{k} \)-points to achieve well converged results. This limitation is overcome using a smearing function to smooth out the discontinuity. To exactly solve the problem at hand, it is important that the final result be extrapolated to the limit where smearing is eliminated. The most common function which meets this criteria is the Methfessel and Paxton function \([139]\) which is used in this work with a smearing width of 0.1 eV.
2.1.6 Computational Details

Having given an overview of the theory of DFT, the parameters used in this work are now presented. Some computational parameters relating to the algorithms used (e.g., energy convergence criteria) are outlined in section 2.2.

To recap the parameters for which convergence tests have already been presented, simulations were performed using the Castep code [136, 137]. k-point grids of spacing 0.02 and 0.012 Å⁻¹ were used for defect calculations and phonon calculations respectively, ultra-soft pseudopotentials [129] with cutoff energy 480 and 660 eV were used in conjunction with Castep 6 and 8 respectively and Methfessel and Paxton [139] smearing is used for metals with a smearing width of 0.02 eV. The scaling factor for the Fast Fourier Transform (FFT) grid and for augmentation charges were set to 2.0 and 2.3 respectively.

For defect calculations, supercell size must be carefully converged to minimise long range elastic interactions between defects but also to manage the computational cost of the simulations. For the Be₁₂M structure, supercell size convergence for the V₇M defect (which has a large defect volume and thus strain field) is shown in figure 2.4. It can be seen that excellent convergence, to around 10⁻² eV, is achieved with a 2×2×2 supercell for all materials. Thus, this supercell size was chosen for defect calculations in the Be₁₂M structure, and a similar number of atoms used (208) with approximately isotropic cell dimensions for defect calculations in other structures.

With respect to phonon calculations, the 2×2×2 Be₁₂M cell is the largest that could be investigated practically using the computational resources available, and thus was
Figure 2.4: Supercell size energy convergence for a $V_M$ defect in the Be$_{12}M$ structure with respect to a $3\times3\times3$ supercell (containing 702 atoms).

used for all phonon calculations with the supercell method. Where other materials were investigated, a supercell with at least 200 atoms was used.

### 2.2 Static Techniques

Static techniques are those that (unlike molecular dynamics) employ no concept of temperature. They are less computationally demanding than dynamic simulations with comparable number of atoms, and in this thesis are used primarily in conjunction with DFT, although can equally be used with empirical potentials. As such, their application to DFT simulations will be focused on in this section.

The simplest static technique is a calculation of the enthalpy of the system, whereby the energy contributions from the electron density are evaluated for a given spatial arrangement of atoms. More common is static energy minimisation, whereby the po-
sitions of the atoms and dimensions of the cell are relaxed to a local energy minimum. This is achieved using an iterative algorithm to move each atom in the system to a position which minimises the total system energy, $E$, contributed from the electron density.

In this work the conjugate gradient mechanism with a Broyden-Fletcher-Goldfarb-Shanno (BFGS) Hessian [140] updating scheme is used for energy minimisation. The direction and distance an atom is moved during a single iteration is determined by the gradient of the energy hypersurface, with the direction given by the force vector and magnitude by the second derivative. As the atomic positions evolve during this process, the energy surface also evolves and thus must be recalculated for each iteration. Complete convergence is achieved when the energy difference between two steps falls to zero. In practice this is unlikely to occur as the closer to the local minima the configuration becomes, the lower the forces and thus lower the magnitude of geometry change. As such, a cutoff energy must be specified, so that when the energy change between steps falls below this value, the simulation is considered converged.

In addition to atomic positions, cell dimensions may also be minimised in this way. In this work, for general geometry optimisations and defect calculations an energy cutoff of $10^{-7} \text{ eV/atom}$ was used, a force cutoff of $0.01 \text{ eV/Å/atom}$ and stress tolerance of $0.01 \text{ eV/Å/atom}$. For phonon calculations, stricter values of $10^{-9} \text{ eV/atom}$, $10^{-4} \text{ eV/Å/atom}$ and $10^{-3} \text{ eV/Å/atom}$ were used respectively.

The main application of static methods in this work is to calculate the formation enthalpy of a defect by comparing the energy of a defective cell $E_{\text{DFT}}^{\text{d}}$ to the perfect cell $E_{\text{DFT}}^{\text{p}}$ and the appropriate reference state of species added or removed $\mu(i)$:

$$E_f = E_{\text{DFT}}^{\text{d}} - E_{\text{DFT}}^{\text{p}} \pm \sum_i \mu(i)$$  \hspace{1cm} (2.19)
Care must be taken to choose an appropriate supercell size (see section 2.1.6) to limit the effects and energy contributions of long range elastic interactions across periodic boundaries. In a similar way, the formation enthalpy ($E_F$) of a given phase can be calculated:

$$E_F = E_{p}^{DFT} - \sum E_{r}^{DFT}$$  \hspace{1cm} (2.20)

where $E_{p}^{DFT}$ is the enthalpy of the phase of interest, and $\sum E_{r}^{DFT}$ is the total enthalpy of the elemental reference states. This allows comparison of the relative stability of different crystal structures and phases, which can be used to predict whether they are likely to be observed experimentally.

### 2.2.1 Transition State Search and Nudged Elastic Band

Geometry optimised cells can also be used as the starting points for transition state searches. Transition state searches are a way to determine the barrier to a chemical reaction or the pathway and energy a diffusing species is most likely to take. In a crystal, the atoms can be visualised as occupying a periodic array of energy wells. For an atom to move to a new position, it must surmount a ridge of higher potential energy before it can occupy a new stable (or metastable) state at the bottom of an energy well. Usually, the atom will cross the ridge at its lowest point (the saddle point), therefore it is imperative to determine where this is and the potential energy of the system relative to the ground state as the atom transits this point, as this provides an approximation of the hopping energy ($E_{hop}$) during diffusion.

To gain a first approximation of the energy at the saddle point, it is useful to perform a Linear Synchronous Transit (LST) search [141]. In the LST method, the energy of the system is calculated for a series of atomic positions which are linearly interpolated
between the reactants and products, with the highest energy replica taken as the saddle point. As there is no guarantee that the saddle point is along a linear interpolation of points, this can at best be taken as an upper bound for the transition energy. This can be improved by performing a constrained orthogonal optimisation of the saddle point, that is to say, the position of the LST maximum is optimised while maintaining the same reaction coordinate/relative separation from the product and reactant. This is augmented by the Quadratic Synchronous Transit (QST) method [141], in which a quadratic interpolation is performed through the reactant, product and LST maximum. The energy maximum along this pathway is then used as the QST prediction of the transition state.

While the QST method usually provides a good description of the transition state, there is no guarantee that the minimum energy pathway (MEP) follows a quadratic trajectory. If it is desirable to find the full MEP rather than just the transition state, it is necessary to use another technique, in this case the Nudged Elastic Band (NEB) method [142]. In the NEB method, a number of replicas are created along a pathway between the reactants and products. If a LST/QST simulation has already been performed, one of these replicas is taken as the identified transition state to speed up convergence. The replicas must be energy minimised to find the MEP, however doing so will inevitably cause the replicas to converge back to the metastable product or reactant. To prevent this, a spring force is applied parallel to the reaction pathway, $\tau ||$. This in itself has been used in the precursor to NEB, the Plain Elastic Band (PEB) method [143], however it is itself not sufficient to ensure the MEP is found. This is because where the MEP is not a linear path between the reactants and products, the spring force effectively acts to minimise the path length which results in the identified path cutting the corner of the true MEP (see figure 2.5). This is exacerbated for higher spring forces, however lowering the spring force causes the replicas around the saddle
point to relax towards the reactant or product resulting in a loss of resolution in this region. The solution is to add a force perpendicular to the path to counteract the parallel spring force, effectively decoupling the dynamics of the path from the particular distribution of images chosen in the discrete representation of the path. The total force on each replica is therefore given by equation 2.21.

\[ F_i^0 = -\nabla V(R_i)_{\perp} + F_i^s \cdot \tau_{||} \]  

(2.21)

\[ \nabla V(R_i)_{\perp} = \nabla V(R_i) - \nabla V(R_i) \cdot \tau_{||} \]  

(2.22)

where \( \tau_{||} \) is the unit tangent to the path.

Figure 2.5: Sketch of possible PEB (red line) and NEB (blue dashed line) results on an imaginary energy landscape with a highly non linear minimum energy pathway. Without the restorative perpendicular spring force, the PEB pathway is dragged away from the minimum energy pathway by the parallel spring force.

These techniques have several limitations, the most limiting being that the spatial arrangement of the reactant and product must be known, which is not always the case. Further, if the initial guess for the MEP is far from the true MEP, these techniques may find a meta MEP (i.e. not the true MEP but a pathway with higher energy). Finally, previous studies have shown that these methods may fail to fully capture complex migration mechanisms where several atoms migrate in concert [108]. Where this is
the case, an entirely different approach using molecular dynamics (MD) to observe the migration mechanism can be used, although this has its own limitations in that it is impractical using DFT (due to being computationally intensive) and cannot capture low temperature migration mechanisms. Full details of the implementation of these methods in the Castep code are outlined in [144].

### 2.2.2 Phonons: Harmonic and Quasi-Harmonic Approximations

The vibrational behaviour of a material constitutes significant contributions to the enthalpy and entropy at finite temperature. As such, understanding the phonons in a material is necessary in order to apply results calculated using static simulation techniques to real world problems. In this work, phonons are treated using the harmonic and quasiharmonic methods. These methods approximate the crystal as a series of symmetrical harmonic oscillators. In reality, the potential energy surface about an atom is unlikely to be completely symmetrical, hence as the energy of the system increases the space an atom can explore through thermal vibrations increases asymmetrically leading to thermal expansion. This approximation is valid for low temperatures where atomic displacement from equilibrium is small and allows the calculation of several useful quantities to a high degree of accuracy.

One quantity that may be calculated is the Zero Point Energy (ZPE). This arises as atoms have small enough mass that quantum mechanical effects are important, in that the atom may only occupy discrete wave functions with non-zero energy, the fundamental representing the effective ground state. The ZPE is the energy difference between this state and the classical description of the system, in which the atom simply sits at the bottom of the potential well. While inconsequential for massive atoms
such as tungsten, the ZPE can be significant for less massive atom such as hydrogen and beryllium.

The contribution of vibrational enthalpy to the total energy of a fixed volume system can be calculated using the harmonic approximation. In this approximation, the lattice parameters of the crystal are fixed, the contributions of the vibrational enthalpy $H_{\text{vib}}(T,V)$, which includes the ZPE, and vibrational entropy $S_{\text{vib}}(T,V)$ are evaluated by integrating across the phonon density of states and phonon energy (according to Bose-Einstein statistics). Combined with the formation enthalpy ($H_F$), these contributions constitute the Helmholtz free energy:

$$F(R,V) = H_F + H_{\text{vib}}(T,V) + S_{\text{vib}}(T,V)$$

The quasi-harmonic method is essentially an extension of the harmonic approximation to model systems with a variable lattice parameter (i.e. constant pressure rather than constant volume). In this method, the potential wells are modelled as being harmonic as in the harmonic approximation, but calculations are repeated for several lattice volumes close to the ideal to characterise the energy wells at each lattice volume. For each temperature an equation of state is then fitted to the data to determine the lowest energy volume, in this case the third order Birch-Murnaghan equation of state:

$$E(V) = E_0 + \frac{9}{16}K_0 V_0 \left\{ \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^{\frac{3}{2}} K'_0 - 6 \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \left[ \frac{2}{3} \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}$$

In this manner, the phonon contribution to the Gibbs free energy is estimated from the contribution to the Helmholtz free energy at varying volumes:

$$G(T,P) = V_{\text{min}}(F_{\text{phonon}}(T,P))$$
To calculate the phonon density of states for a material, the force constants matrix must be evaluated. This is achieved using the supercell method, in which positions of the atoms are slightly perturbed and the reaction forces calculated. A supercell must be used due to long range elastic interactions in crystalline solids, although the use of a supercell is not necessary for molecules.

### 2.3 Empirical Potentials

In addition to DFT, classical potentials are another way to describe the energy of a simulated atomic system. In this case, it is assumed that the energy of the system can be evaluated by summating pairwise interactions between atoms. This approach has an advantage over DFT in that it is considerably less computationally expensive since the computational cost scales linearly with the number of atoms. Consequently, this description can be used to access much greater length and timescales, on the order of $1 \, \mu m^3$ and $10^3 \, ns$ compared to $1 \, nm^3$ and $1 \, ns$ for DFT.

In this work, a classic Born description of the lattice is used, whereby ions are treated as infinitesimally small points acting under pairwise interactions. Typically, these interactions consist of a short range pairwise potential, $\Phi_{ab}(r_{ij})$ and a long range coulombic interaction. This thesis examines only metallic and covalent systems, thus the coulombic term can be discounted and the total energy of the system described as the summation of all short range potentials:

$$E = \frac{1}{2} \sum_i \sum_{i \neq j} \Phi_{ab}(r_{ij}) \quad (2.26)$$

where $r_{ij}$ is the interatomic separation of atoms $i$ and $j$ which are species $a$ and $b$ respectively. An iconic and widely used short range potential is the Morse potential [145],
Figure 2.6: Morse potential for tungsten, utilised as part of the bond order potential set derived by Juslin et al. [146]. $D_e = 5.419$ eV and $r_e = 2.341$ Å.

which has the form:

$$\Phi_{ab}(r) = D_e \left(1 - e^{-\alpha(r_{ij} - r_e)}\right)^2$$

(2.27)

where $D_e$ is the dissociation energy of the dimer, $r_e$ is the equilibrium bond length, and $\alpha$ is the force constant. The Morse functional has been widely used in part due to its intuitive form, insofar that each constant is related to a physical concept (as depicted in figure 2.6), and moreover can be parameterised explicitly from experimental results [145]. Further, this potential form can provide a reasonable description of simple systems such as dimers and some FCC metals.

### 2.3.1 Embedded Atom Method

Despite the success of simple pairwise potentials, they are inadequate to describe certain systems, in particular those materials in which bonding is strongly directional. This is the case for HCP metals where the $c/a$ ratio deviates from the ideal of 1.633. Beryllium for example has a $c/a$ ratio of 1.56(7) [122]. Covalently bonded materials
such as carbon and tungsten carbide also have strongly directional bonds. As such, several approaches have been developed to incorporate the local environment into potential forms, the most widely used of which are Embedded Atom Method (EAM) potentials developed by Daw and Baskes [147, 148].

In the EAM model atoms are treated as points acted on by pairwise potentials, but also include a function to describe the electron density around the atom, $\rho_i(r_{ij})$. The contribution of the electron density, $\rho_i$, to the potential energy, $E_i$, of atom $i$ experiencing it is described by the embedding function, $F(\rho_i)$. Thus, the total energy of the system can be determined from:

$$E_{ij} = \frac{1}{2} \sum_i \sum_{i \neq j} \Phi_{ab}(r_{ij}) + F_i(\rho_i(r_{ij}))$$ (2.28)

The electron density at atom $i$, $\rho_i$, is the summation of contributions from all surrounding atoms. As such, provided the embedding function is not linear, the pairwise density functions cannot be deconvoluted from each other, making this a many body potential.

### 2.3.2 EAM Potential for Beryllium

In this thesis, the EAM potential form developed and parametrised by Agrawal et al. [149] was used to simulate pure beryllium as it accurately reproduces many physical properties of pure beryllium, notably the self-interstitial and vacancy energies, which are important for threshold displacement simulations. An overview of these properties compared to experimental values and those predicted by other potentials (including Modified EAM (MEAM) and Bond Order Potentials (BOP)) is presented in table 2.2. The BOP by Björkas et al. is also used to simulate beryllium, and is outlined in section
2.3. Empirical Potentials

For the Agrawal parametrisation of the EAM formalism, the pair potential is a Morse potential, identical to equation 2.27. The electron density function, $\rho_i(r_{ij})$, is a simple exponential:

$$\rho(r_{ij}) = Ae^{B(r_{ij} - r_c)}$$  \hspace{1cm} (2.29)

where $A$ and $B$ are constants. To both the pair potentials and the electron density function, the Voter taper function [154] is applied, which for the pair potentials is:

$$\Phi_{\text{tapered}} = \Phi(r) - \Phi(r_c) + \frac{r_c}{m} \left[ 1 - \left( \frac{r}{r_c} \right)^m \right] \frac{d\Phi}{dr} \bigg|_{r_c}$$  \hspace{1cm} (2.30)

where $r_c$ is the cutoff radius, and $m$ is a constant. This cutoff function effectively limits the interaction of the pair potentials and electron density and prevents a discontinuity in the derivative of the energy gradient which would make the simulation unstable.

The embedding function used is the Johnson Function [155, 156]:

$$F = F_0 \left[ 1 - \ln \frac{\rho_i}{\rho_0} \beta \right] - F_1 \frac{\rho_i}{\rho_0} \gamma$$  \hspace{1cm} (2.31)

Where $\beta, \gamma$, $F_1$ and $F_0$ are empirically derived constants. The functional form of the pair potentials, density function and embedding function, as parameterised for pure beryllium using the constants outlined in table 2.3 are shown in figure 2.7.

It can be seen that the Johnson function has a minimum with respect to reduced electron density, thus subtly shifting the overall minimum position in the energy function between two atoms when more atoms are added. This has the effect of stabilising the HCP crystal structure, and altering the $c/a$ ratio from the ideal of 1.633 to 1.568 which is the experimental value for pure beryllium. To achieve this, it is necessary to use quite a large cutoff (5 Å) which makes this potential more computationally expensive.
Table 2.2: Selected experimental and DFT data compared to that predicted by the Agrawal potential and several other available atomic potential sets for the simulation of beryllium. Δ% is the % difference from experimental values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Exp.\textsuperscript{a} value</th>
<th>Δ%</th>
<th>EAM\textsuperscript{a} value</th>
<th>Δ%</th>
<th>EAM\textsuperscript{b} value</th>
<th>Δ%</th>
<th>MEAM\textsuperscript{c} value</th>
<th>Δ%</th>
<th>MEAM\textsuperscript{d} value</th>
<th>Δ%</th>
<th>MEAM\textsuperscript{e} value</th>
<th>Δ%</th>
<th>ABOP\textsuperscript{f} value</th>
<th>Δ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>E\textsubscript{c} (eV)</td>
<td>3.32</td>
<td>0.60</td>
<td>3.34</td>
<td>3.70</td>
<td>3.43</td>
<td>3.31</td>
<td>-</td>
<td>-</td>
<td>3.43</td>
<td>3.31</td>
<td>3.32</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{11} (GPa)</td>
<td>294</td>
<td>-1.02</td>
<td>291</td>
<td>-69.73</td>
<td>3.62</td>
<td>-98.77</td>
<td>259</td>
<td>-11.90</td>
<td>331</td>
<td>12.59</td>
<td>280.5</td>
<td>-4.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{33} (GPa)</td>
<td>357</td>
<td>0.00</td>
<td>257</td>
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<td>329</td>
<td>-7.84</td>
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<td>-13.45</td>
<td>349.7</td>
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<tr>
<td>C\textsubscript{12} (GPa)</td>
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<td>96.30</td>
<td>53</td>
<td>-59</td>
<td>-318.52</td>
<td>88</td>
<td>225.93</td>
<td>77</td>
<td>185.19</td>
<td>-11</td>
<td>140.74</td>
<td>58.6</td>
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<tr>
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<td>10</td>
<td>-37</td>
<td>-364.29</td>
<td>-22</td>
<td>-257.14</td>
<td>9</td>
<td>-35.71</td>
<td>18</td>
<td>28.57</td>
<td>13.5</td>
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<td></td>
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<tr>
<td>C\textsubscript{44} (GPa)</td>
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<td>-23.46</td>
<td>124</td>
<td>-33.95</td>
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<td>19</td>
<td>-88.27</td>
<td>198.2</td>
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</tr>
<tr>
<td>C\textsubscript{66} (GPa)</td>
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<td>119</td>
<td>-44.36</td>
<td>137</td>
<td>3.01</td>
<td>91</td>
<td>-31.58</td>
<td>171</td>
<td>28.57</td>
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<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (GPa)</td>
<td>117</td>
<td>3.42</td>
<td>121</td>
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<td>-4.27</td>
<td>115</td>
<td>-1.71</td>
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<td>-3.42</td>
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</tr>
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<td>G (GPa)</td>
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<td>129</td>
<td>2.00</td>
<td>137</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td></td>
</tr>
<tr>
<td>E\textsubscript{f}(V)(eV)</td>
<td>0.85</td>
<td>1.26</td>
<td>1.26</td>
<td>48.24</td>
<td>1.13</td>
<td>32.94</td>
<td>1.23</td>
<td>44.71</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}: Agrawal et al. [149] \textsuperscript{b}: Kaimi et al. [150] \textsuperscript{c}: Baskes and Johnson [151] \textsuperscript{d}: Thompson et al. [151] \textsuperscript{e}: Dremov et al. [152] \textsuperscript{f}: Björkas et al. [153]
2.3. Empirical Potentials

Figure 2.7: a) Morse and tapered Morse potential. b) Electron density as a function of \( r_{ij} \). c) Johnson density functional. All functions and functionals parameterised for beryllium using the values in table 2.2.

than many other EAM potentials, though considerably less so than even the simplest Modified EAM potentials.

2.3.3 Bond Order Potentials

In addition to EAM potentials, another family of potentials has been developed to overcome the limitations of simple pairwise potentials. Bond Order Potentials (BOP) are based on Abell’s bond order concept [157], which relates the strength of the bond between two atoms to the number of neighbours: the more neighbours the weaker the bond. In this way it is similar to EAM potentials, and for some parameterisations is functionally identical. The generalised form of a BOP potential is:

\[
E_{ij} = \frac{1}{2} \sum_{i \neq j} f_{ij}^c(r_{ij}) \left[ \Phi_{ij}^R(r_{ij}) - b_{ij} \Phi_{ij}^A(r_{ij}) \right] \tag{2.32}
\]

where \( f_{ij}^c(r_{ij}) \) is a cutoff function which limits the interaction to nearby atoms, \( \Phi_{ij}^R(r_{ij}) \) and \( \Phi_{ij}^A(r_{ij}) \) are repulsive and attractive contributions to the pairwise potential respectively and \( b_{ij} \) is the bond order term. \( f_{ij}^c(r_{ij}) \) is necessary to limit the number of other atoms each atom interacts with without introducing a discontinuity in the derivative of
Table 2.3: Parameters for the EAM function parameterised by Agrawal et al. [149] for pure beryllium.

<table>
<thead>
<tr>
<th>Function</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pair potential function</td>
<td>(D_e) (eV)</td>
<td>0.412 46</td>
</tr>
<tr>
<td></td>
<td>(\alpha) (Å(^{-1}))</td>
<td>0.363 24</td>
</tr>
<tr>
<td></td>
<td>(r_e) (Å)</td>
<td>2.290 00</td>
</tr>
<tr>
<td>Electron density function</td>
<td>A</td>
<td>1.597 00</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.497 13</td>
</tr>
<tr>
<td>Embedding function</td>
<td>(F_o) (eV)</td>
<td>2.039 30</td>
</tr>
<tr>
<td></td>
<td>(F_1) (eV)</td>
<td>-12.6178</td>
</tr>
<tr>
<td></td>
<td>(\beta) (unitless)</td>
<td>0.187 52</td>
</tr>
<tr>
<td></td>
<td>(\gamma) (unitless)</td>
<td>-2.288 27</td>
</tr>
<tr>
<td>Voter function</td>
<td>(m) (unitless)</td>
<td>10.0000</td>
</tr>
<tr>
<td></td>
<td>(r_c(\text{Å}))</td>
<td>5.0000</td>
</tr>
</tbody>
</table>

the potential energy, otherwise computational requirements would be impossibly large. The bond order term, \((b_{ij})\), includes three body effects similarly to the EAM function, and may also include an implicit angularity term. When such a term is included, this potential form can be considered broadly analogous to MEAM potentials.

Due to their ability to model bond breaking and directional bonds, BOPs are widely employed to model covalent systems and organic processes where these properties are important. Further, given their functional similarity to EAM and MEAM potentials they can provide a good description of metallic systems, particularly those in which angular effects are important.

2.3.4 Bond Order Potentials for the Tungsten - Carbon System and Beryllium

In this thesis bond order potentials developed by Tersoff et al. [158] and parametrised by Brenner et al. [159, 160] for carbon, Juslin et al. [146] for tungsten, and Björkas et
2.3. Empirical Potentials

Table 2.4: Materials properties of tungsten, carbon and mixed tungsten-carbon materials. Experimental and DFT data are included for comparison [146].

<table>
<thead>
<tr>
<th></th>
<th>Wa exp.</th>
<th>DFT</th>
<th>BOP</th>
<th>W-Ca exp.</th>
<th>DFT</th>
<th>BOP</th>
<th>Cb exp.</th>
<th>BOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimer</td>
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<td></td>
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<td></td>
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<tr>
<td></td>
<td>E_c</td>
<td></td>
<td></td>
<td>E_c</td>
<td></td>
<td></td>
<td>E_c</td>
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<tr>
<td></td>
<td>r_0</td>
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<td></td>
<td>r_0</td>
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<td>r_0</td>
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<td></td>
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</tr>
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<td></td>
<td>E_c</td>
<td></td>
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<td>E_c</td>
<td></td>
<td></td>
<td>E_c</td>
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</tr>
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<td>a</td>
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<td>B</td>
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</tr>
<tr>
<td></td>
<td>B'</td>
<td></td>
<td></td>
<td>B'</td>
<td></td>
<td></td>
<td>B'</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c_{11}</td>
<td></td>
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<td>c_{11}</td>
<td></td>
<td></td>
<td>c_{11}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c_{12}</td>
<td></td>
<td></td>
<td>c_{12}</td>
<td></td>
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<td>c_{12}</td>
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</tr>
<tr>
<td></td>
<td>c_{44}</td>
<td></td>
<td></td>
<td>c_{44}</td>
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<td>c_{44}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E_{h(V)}</td>
<td></td>
<td></td>
<td>E_{h(V)}</td>
<td></td>
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</tr>
</tbody>
</table>

al. [161] for beryllium, are used to model the tungsten - carbon system and beryllium. These potentials have been developed to be consistent with a larger potential set developed by K. Nordlund et al. [146, 161, 153, 162] to treat all species common in a nuclear fusion environment. As such it would be possible to extend this work to other fusion materials without great difficulty. These potentials have been developed explicitly for non-equilibrium processes, so that, as well as accurately reproducing equilibrium properties, they also provide a good description of defects, and even molecular species as shown in table 2.4 for tungsten-carbon and table 2.2 for beryllium.

The Brenner, Juslin and Björkas potential parametrisations are based on the Tersoff potential form [158]. In this potential form, the attractive and repulsive terms of equation 2.32 are Morse like terms:

\[
\Phi_{ij}^R = \frac{D_e}{S-1}\exp(-\beta\sqrt{2s(r_{ij} - r_e)})
\]  

(2.33)
\[ \Phi_{ij}^A = \frac{SD_e}{S-1} \exp(-\beta \sqrt{2s}(r_{ij} - r_e)) \] (2.34)

where \( \beta \) can be calculated from the ground state oscillation frequency of the dimer and S is an empirical constant. The cutoff function, \( f_{ij}^c(r) \) is given by:

\[
f_{ij}^c(r) = \begin{cases} 
1, & r \leq R - D, \\
\frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2} \left(\frac{r - R}{D}\right)\right), & |R - r| \leq D, \\
0, & r \geq R + D
\end{cases}
\] (2.35)

where R and D are empirical constants chosen to restrict interaction to the nearest and second nearest neighbour sphere. The bond order term, \( b_{ij} \) includes both three-body terms (analogous to EAM) and an explicit angular term, \( g(\theta) \):

\[ b_{ij} = (1 - \chi_{ij})^{-1/2} \] (2.36)

\[ \chi_{ij} = \sum_{k(\neq i,j)} f_{ik}^c(r_{ik}) g_{ik}(\theta_{ijk}) \omega_{ijk} e^{\alpha_{ijk}(r_{ij} - r_{ik})} \] (2.37)

\[ g(\theta) = \gamma \left(1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h + \cos\theta)^2}\right) \] (2.38)

where \( \omega, \alpha, \gamma, c, d \) and \( h \) are empirical constants. The cutoff function \( f_c(r) \) is also applied to the three bond terms to prevent spurious non-physical interactions between distant atoms. The empirical parameters used in this parameterisation for carbon, tungsten and mixed interactions are shown in table 2.5.

One significant limitation of this potential form is that it does not include an explicit dispersion term, and therefore cannot accurately describe van-der-Waals forces [163]. While these forces are negligible in bulk tungsten, tungsten carbide and diamond, they are significant in graphite in that they are the main interaction between graphene sheets [164]. Despite this, simulations of graphite with this potential show that it can...
Table 2.5: Parameters for the Tersoff potential [158] parameterised by Brenner et al. [159, 160], Juslin et al. [146] and Björkas et al. [153] for tungsten, tungsten-carbon, carbon and beryllium.

<table>
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<tr>
<th>Parameter</th>
<th>W-W</th>
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<th>C-C</th>
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<td>1.0</td>
<td>0.82657999</td>
</tr>
<tr>
<td>R (Å)</td>
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<td>2.80</td>
<td>1.85</td>
<td>2.685</td>
</tr>
<tr>
<td>D (Å)</td>
<td>0.3</td>
<td>0.2</td>
<td>0.15</td>
<td>0.223</td>
</tr>
</tbody>
</table>

make a good approximation of most ground state and equilibrium properties, indicating there is some force between graphene sheets, however the sheets tend to glide over one another. Thus, results in graphite using these potentials must be treated with caution.

### 2.3.5 ZBL modifications

Most empirical potentials, pairwise, EAM or BOP, are selected and parameterised to reproduce equilibrium properties of materials and molecules. These include elastic constants, lattice parameters and phonons, which are needed to accurately predict phenomenon of interest in materials. In practical terms, this means that potentials usually provide a good description around the bottom of the potential well. This does not guarantee that the potential will accurately predict states far from equilibrium if such states have not been included in the fitting process. In particular, many potentials are unphysical for very small interatomic separations, as may occur during (high kinetic energy) threshold displacement or damage cascade simulations.
This shortcoming is overcome using the Ziegler-Biersack-Littmark (ZBL) potential [110] which models nuclear repulsion screened by electrons, and has the form:

$$\Phi_{ij}^{ZBL} = \frac{1}{4\pi\epsilon_0} \frac{Z_i Z_j e^2}{r_{ij}} \phi(r_{ij}/a)$$ (2.39)

$$a = \frac{0.46850}{Z_i^{0.23} + Z_j^{0.23}}$$ (2.40)

$$\phi(x) = 0.18175e^{-3.19980x} + 0.50986e^{-0.94229x}$$

$$+0.28022e^{-0.40290x} + 0.02817e^{-0.20162x}$$ (2.41)

Where $Z_i$ and $Z_j$ are the atomic number of the two species, $e$ the electron charge and $\epsilon_0$ the permactivity of free space. This potential has the advantage that it is dependent only on the atomic number of the atoms, and thus contains no fitted constants. The ZBL potential replaces the pairwise component of an empirical potential at short interatomic separations and is splined to the empirical potential with a switching function that ensures there is no discontinuity in the second derivative of the overall potential form. In the case of the bond order potential described above, the pairwise component is modified with the ZBL potential using the function:

$$\Phi_{mod}^V = \Phi^{ZBL}(r)[1 - F(r)] + \Phi^R(r)F(r)$$ (2.42)

$$F(r) = \frac{1}{1 + e^{-b(r-r_f)}}$$ (2.43)

$B_f$ and $r_f$ are empirical constants, in this case fit to create a smooth spline to DFT data (which has been shown to accurately predict interatomic repulsion). The parameters for the tungsten - carbon system are outlined in table 2.6.
2.4 Molecular Dynamics

Molecular Dynamics (MD) is a simulation technique in which the positions of atoms are allowed to evolve over time, thereby allowing for the effective simulation of temperature. The simulation proceeds as a series of discreet timesteps $\delta t$, with the evolution of each atom’s acceleration, velocity and position between time $t$ and $t+\delta t$ calculated from Newton’s equations of motion outlined in equation 2.44. The force, $F_i$ is calculated from the gradient of the potential energy surface $\nabla \Phi_i$ as evaluated using empirical potentials, or in the case of quantum-MD, DFT.

$$\ddot{r}(t) = \frac{F_i(r(t))}{m_i} = -\nabla \Phi_i(r(t))$$

Using these equations, the velocities and positions at $t+\delta t$ are calculated using the velocity verlet integration method [165, 166], which is computationally efficient, numerically stable and conserves the overall energy of the system (providing a sensible timestep is chosen). In this method, the second order equation of motion is split into two first order differential equations, $a = \frac{dv}{dt}$ and $v = \frac{dx}{dt}$ which then undergo a taylor expansion to give:

$$r(t + \delta t) = r(t) + \delta t \dot{r}(t) + \frac{\delta t^2}{2} \ddot{r}(t) + O\delta t^3$$

Table 2.6: Parameters for the ZBL switching function for tungsten, tungsten-carbon, carbon and beryllium [146, 153].

<table>
<thead>
<tr>
<th></th>
<th>W-W</th>
<th>W-C</th>
<th>C-C</th>
<th>Be-Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_f$(Å)</td>
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<td>1.2</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>$b_f$(1/Å)</td>
<td>12</td>
<td>7</td>
<td>8</td>
<td>7</td>
</tr>
</tbody>
</table>
\[
\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \delta t \mathbf{\dot{v}}(t) + \frac{\delta t^2}{2} \mathbf{\ddot{v}}(t) + O(\delta t^3)
\]  
(2.46)

The second derivative of velocity \( \mathbf{\ddot{v}}(t) \) is the only value that cannot be defined in terms of known quantities, but it can be calculated through a Taylor expansion of \( \mathbf{\dot{v}}(t) \), which can then be substituted into the original equation to give:

\[
\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2} \delta t^2 \mathbf{a}(t)
\]  
(2.47)

\[
\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \frac{1}{2} \delta t \left[ \mathbf{a}(t) + \mathbf{a}(t + \delta t) \right]
\]  
(2.48)

From these equations in conjunction with equation 2.44, the trajectory of atoms at \( t + \delta t \) can be calculated from the atomic position, velocity and acceleration, whereby equation 2.47 is first used to calculate the new positions, equation 2.48 to calculate acceleration, and the force calculated as \( \Delta \Phi_i \).

A key consideration when performing MD simulations is the length of the timestep \( \delta t \). Too long a timestep and the simulation may become unphysical, with atomic trajectories deviating significantly from those for an infinitesimally small timestep. Particular consideration of the timestep must be made when investigating energetic phenomena such as radiation damage, as deviation from the results of an infinitesimally small timestep increases with increasing velocity and acceleration of the simulated atoms. As such, it is desirable to use a much shorter timestep when performing such simulations. There is however a strong pressure to maximise \( \delta t \) as computational intensity increases linearly with decreasing timestep. Typically, for most systems simulated around terrestrial temperatures (0 - 3000 K), it has been found that a timestep of 1 - 4 fs is adequate to maintain the integrity of the simulation while minimising computational cost. This allows total simulation times on the order of \( 10^{-7} \) seconds, which is still somewhat limited by comparison to many phenomena of interest.
2.4. Molecular Dynamics

An additional consideration for the practical implementation of MD is how to introduce the concepts of temperature and pressure, which of course are important quantities for a real experiment. To relate the atomic trajectories of an MD simulation to such macroscopic properties, statistical mechanics is applied through the use of a thermodynamic ensemble. A thermodynamical ensemble represents all possible states of a system that have a set of common extrinsic properties. In MD simulations, unless accounting for transmutation, it is implicit that the number of atoms, $N$, remains the same. Further, if the volume, $V$, is fixed, and no energy, $E$, is artificially added or subtracted from the system, then the state of the system at each timestep can be said to be a member of the NVE micro canonical ensemble.

To calculate macroscopic properties, an ensemble average is taken, whereby an observable value is averaged over all states of the system with a weighting factor in favour of low energy states. This ensures that the bulk properties are averaged according to the time spent in a given state. In practice, the states accessed in a MD simulation are already effectively weighted according to the probability of being found in a particular state, thus it is sufficient only to take an average of states sampled over a sufficient number of timesteps.

In addition to the NVE ensemble, it may be useful to control temperature, $T$, and pressure, $P$, as simulations often aim to mimic conditions of interest that occur at a range of temperatures and pressures. This leads to the additional NPT (number, pressure, temperature) and NVT (number, volume, temperature) ensembles. Temperature is controlled using a thermostat, which scales the velocity of the simulated atoms to maintain near constant temperature. Many thermostats use the concept of an external heat bath to which the simulation is weakly coupled and thus energy can flow with
characteristic relaxation time, thereby gradually restoring the simulation to the desired temperature. The relaxation time must be carefully selected to avoid resonant effects. Similarly, a barostat scales the volume of the cell deterministically to maintain constant pressure. Finally, similarly to static simulations, to simulate the bulk material, periodic boundaries must be employed. In this work the Nose-Hoover thermostat and barostat [167, 168, 169] and Berendsen barostat [170] are used in conjunction with the NPT and NVT ensembles respectively for thermal equilibration of supercells. All MD simulations in this work are implemented in the LAMMPS code [171].

2.5 Inelastic Neutron Scattering

Inelastic neutron scattering is a technique that can be used to probe the structure and vibrational states of materials. Radiation can interact with matter either elastically, where the total kinetic energy of the system is conserved, or inelastically where energy is transferred. The latter includes many possible interactions, such as Compton scattering (where energy is transferred from a photon to an electron), nuclear excitation and phonon interactions. The latter of these simultaneously probes the structure and dynamics of the material, and thus provides ample information for comparison with theoretical results (e.g. from DFT).

When a monochromatic neutron beam with flux $\sigma_i$ and wave vector $k_i$ is scattered by a sample, it is useful to examine the differential cross-section and partial differential cross-section relative to the total cross section, $\sigma_T$:

$$\frac{d\sigma}{d\Omega}$$

(2.49)
where \( \sigma \) is the scattered flux, \( \Omega \) the angular area relative to the sample, and \( E_F \) the energy difference between the incident and scattered neutrons. These quantities are related to the geometrical sample set-up in figure 2.9. The differential cross-section probes only the change in momentum of the incident and scattered neutrons, which is dominated by elastic scattering but includes inelastic contributions (although it cannot provide information about the later). The partial differential cross-section provides information about both momentum and energy changes and is therefore useful for probing inelastic scattering. The partial differential cross-section can be integrated to the differential cross-section which can be integrated to the total:

\[
\frac{d^2\sigma}{d\Omega dE_f} = \int \frac{d\sigma}{d\Omega} d\Omega = \int \frac{d^2\sigma}{d\Omega dE_f} d\Omega dE_f
\]

Thus it is clear that the total cross section \( \gg \) differential \( \gg \) partial differential, with the differential cross-section typically \( 10^6 \) times the partial. The partial differential scattering cross-section is composed of two primary contributions, the neutron structure factor \( S(Q, \omega) \) and pair correlation function \( G(r, t) \):

\[
\frac{d^2\sigma}{d\Omega dE_f} = N \frac{k_f}{k_i} \frac{1}{|b|^2} S(Q, \omega)
\]

\[
S(Q, \omega) = \frac{1}{2\pi \hbar} \int G(r, t) e^{i(Q\cdot r - \omega t)} dr dt
\]

\[
G(r, t) = \frac{1}{2\pi} \frac{3}{N} \int \sum_{ij} \sum_{i'j'} e^{iQr} < e^{-iQF_j^{(0)}} e^{iQF_j^{(1)}} > dQ
\]

where \( k \) is the wavevector, \( b \) is an element/isotope dependent constant, \( Q \) is the scattering vector, and \( \omega \) is the frequency. This expression can further be split into contri-
2.5. Inelastic Neutron Scattering

![Graph showing typical neutron scattering mechanisms as a function of energy transfer.](image)

Figure 2.8: Typical neutron scattering mechanisms as a function of energy transfer probed using inelastic neutron scattering spectroscopy. Modified from [172].

butions from coherent (c) and incoherent scattering (i):

\[
\frac{d^2\sigma}{d\Omega dE_t} = \sigma_c S_c(Q, \omega) + \sigma_i S_i(Q, \omega)
\]  \hspace{1cm} (2.55)

Coherent scattering measures the Fourier transform of the pair correlation function (i.e. interference effects such as diffraction and phonons) while incoherent scattering measures the Fourier transform of the self-correlation effect (i.e. single particle scattering). The latter includes the vibrational density of states, which can be compared to that simulated with DFT data. Typical scattering modes as a function of energy transfer are shown in figure 2.8 below.

### 2.5.1 Experimental Setup

In this section a broad overview of the experimental setup is given. Details such as the monochromator used and energy range scanned were changed during the experiment in response to preliminary results, and thus are reported in detail in chapter 3.
For these experiments, the TAIPAN triple axis spectrometer based at the Australian Nuclear Science and Technology Organisation (ANSTO) was used. A schematic of this instrument is shown in figure 2.9. The OPAL reactor provided a source of thermal neutrons. Fast neutrons (around 2 MeV) are moderated through scattering interactions with the D$_2$O that is used to moderate neutrons to lower energies. When fully moderated, the distribution of neutron energies can be considered a Maxwellian distribution for the ambient temperature which is 300 K for the OPAL reactor. It is, however, likely that the source will also include some fast and epithermal neutrons.

A thermal spectrum of neutrons is useful as the average energy (around 82 meV) corresponds to a wavelength (0.2 nm) close to that of the lattice spacing for most crystalline solids, making them useful to probe structural information, for instance through neutron diffraction. Most scattering techniques though, rely on having a monochromatic neutron source. This is achieved using a monochromator, which is usually a single crystal of ultra pure beryllium, copper or graphite. When the thermal neutrons interact with the single crystal, they are diffracted as per Braggs law:

\[ n\lambda = 2d\sin(\theta) \]  

(2.56)

where \( n \) is the order of the reflection, \( d \) the interatomic spacing of the crystal and \( \theta \) the scattering angle. A strong single Bragg reflection is selected, for example for the (100) planes, which produces a spectrum of diffracted monochromatic neutrons which can be scanned over either by rotating the crystal, or in the case of the TAIPAN instrument, the sample around the crystal. This produces a near monochromatic neutron beam, the energy of which can be approximated as a Gaussian distribution with measured full-width-half-maximum (FWHM). Given the uneven distribution of the thermal spec-
trum of neutrons, the maximum intensity of this distribution varies with energy.

The second axis (about the sample in figure 2.9) provides spatial resolution of the scattering about the sample, (i.e. the differential scattering cross-section). This is combined with the third axis, which is a pyrolytic graphite analyser, used to analyse of the energy of the scattered neutron beam. This provides information about the partial differential scattering cross-section, and thus the vibrational density of states. It should be noted that the partial differential cross section measured will contain contributions from other sources, thus care should be taken when comparing to DFT simulated density of states.

Figure 2.9: Schematic of the TAIPAN triple axis spectrometer. Reproduced from [173].
Chapter 3

Structural Investigations of Beryllides

This work is published in:
M. L. Jackson, P. A. Burr, R. W. Grimes “Resolving the Structure of TiBe$_{12}$”, Acta Crystallographica, 72, 277-280 (2016) [174]

3.1 Introduction

As explored in section 1.6, beryllium rich beryllides are candidates to replace beryllium in the first wall and as neutron multipliers in future fusion reactors [56]. Before they can be used in such applications however, their basic materials properties and irradiation behaviour must be well understood and quantified. Due to the toxicity of these materials [175], they have found few applications, and consequently few investigations into their properties have been conducted.
Recently, Be$_{12}$Ti and Be$_{12}$V in particular have been investigated for fusion applications [176], with several experimental studies investigating basic properties such as thermal conductivity [177], thermal expansivity [82] and yield strength [82], as well as irradiation effects [93, 92, 178]. Despite this, significant work remains before they can be qualified for these applications. Notably, and of significance to this work, there remains some uncertainty regarding the crystal structure of Be$_{12}$Ti. While the crystal structures of other Be$_{12}$M (where M is a transition metal) compounds are well defined, to date there is some controversy as to whether Be$_{12}$Ti exhibits a hexagonal or tetragonal structure [179, 95, 180]. This is imperative to establish before proceeding with computational studies, as the validity of the results of such studies are completely predicated on the crystal structure assumed. As such, this is explored in section 3.2.

There is even less experimental data available for other Be$_{12}$M and Be$_{13}$M beryllides. This poses an issue for computational investigations of these materials, as without experimental data, the validation of such investigations is a challenge. Neutron scattering data provides a particularly useful point of comparison for the validation of computational models as it interrogates the vibrational states of the material, and by extension the structure and energy landscape. It is highly desirable to be able to accurately model both of these quantities. As such, in section 3.3, one Be$_{13}$M sample and five Be$_{12}$M samples are investigated using inelastic neutron scattering, and results compared to the simulated phonon density of states.

### 3.2 Resolving the Structure of Be$_{12}$Ti

The crystal structure of Be$_{12}$Ti was first identified by Raeuchle and Rundle in 1949 [181]. Samples were prepared by heating titanium with an excess of beryllium (1:15)
3.2. Resolving the Structure of Be$_{12}$Ti

at 1400°C, resulting in the formation of several small crystals which were then examined with X-ray diffraction (XRD). They identified a large hexagonal unit cell with lattice constants $a = 29.44\pm0.01$ Å and $c = 7.33\pm0.01$ Å. It was reported that this full unit cell could be constructed from several repeating pseudocells which have hexagonal P$_c$/mmm symmetry and lattice constants $a = 4.23$ Å and $c = 7.33$ Å, with atomic coordinates Ti(0,0,0), Be(0,0,0.29), Be($\frac{1}{2}$,$\frac{1}{2}$,0) and Be($\frac{1}{2}$,$\frac{1}{2}$,0.5). In this scheme, the authors identified that titanium is disordered between (0,0,0) and (0,0,$\frac{1}{2}$) in adjacent pseudocells, which made refinement of the beryllium positions impossible.

Subsequently, through X-ray diffraction Zalkin et al. identified Be$_{12}$Ti (along with several other Be$_{12}$M beryllides) as being the tetragonal I$_4$/mmm structure with lattice parameters $a = 7.35$ and $c = 4.19$ Å [89]. The I$_4$/mmm structure, presented in figure 1.14 section 1.6 and reproduced below in figure 3.1, is accepted as the crystal structure for the other Be$_{12}$M compounds investigated in this thesis, namely Be$_{12}$Mo, Be$_{12}$V, Be$_{12}$W, Be$_{12}$Nb and Be$_{12}$Ta, however, some studies continue to cite the P$_c$/mmm pseudo-cell structure identified by Raeuchle and Rundle [181] for Be$_{12}$Ti, and indeed to use it as the basis for density functional theory simulations [95, 180].

Work by Gillam et al. [182] suggested that the P$_c$/mmm phase reported by Raeuchle and Rundle may in fact have been Be$_{17}$Ti$_2$, which has a clear structural relationship with the I$_4$/mmm phase as shown in figure 3.1. In this relation, the $a$ and $c$ parameters of the I$_4$/mmm and P$_c$/mmm phases respectively are swapped, and the position of the titanium site at either (0,0,0) or (0,$\frac{1}{2}$,0) in the tetragonal system is disrupted, with titanium sites at (0,0,$\frac{1}{4}$) and ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{4}$) in the Be$_{17}$Ti$_2$ phase. It is clear that the hexagonal Be$_{12}$Ti pseudo-cell also bears a relation to both structures, differing from the tetragonal phase only in the alternating (0,0,$\frac{1}{2}$) displacement of the titanium site (and consequent perturbation of the beryllium sites).
3.2. Resolving the Structure of Be\textsubscript{12}Ti

Figure 3.1: Left: unit cell of Be\textsubscript{12}Ti viewed in the [001] and [100] directions. Right: correspondence of Be\textsubscript{12}Ti hexagonal pseudocell and Be\textsubscript{17}Ti\textsubscript{2} unit cell with tetragonal Be\textsubscript{12}Ti structure. To achieve Be\textsubscript{17}Ti\textsubscript{2} stochiometry, titanium edge atoms in the Be\textsubscript{17}Ti\textsubscript{2} structure are duplicated at (0,0,\frac{1}{4}) and (0,0,\frac{3}{4}).

Despite the work of Gilliam et al. and Zalkin et al., various studies have continued to reference the existence of the hexagonal P\textsubscript{c}c\textsubscript{1}/mmm phase [95, 180]. While this may not affect the key conclusions of experimental studies (given the close similarities of the hexagonal and tetragonal phases), the validity of DFT simulations (like those performed in this work) is completely predicated on the crystal structure. As such, it is vital that this confusion be resolved before proceeding.

It is likely that the confusion between these phases has persisted due to their close structural similarities and by extension, similar diffraction patterns. Simulated diffraction patterns from DFT data for the P\textsubscript{c}c\textsubscript{1}/mmm Be\textsubscript{12}Ti, I\textsubscript{4}/mmm Be\textsubscript{12}Ti and P\textsubscript{c}c\textsubscript{1}/mmm Be\textsubscript{17}Ti\textsubscript{2} structures, as well as pure Be, which is expected to be a common contaminant in XRD samples, are presented in figure 3.2.

There is a strong correspondence between the diffraction patterns of the tetragonal cell...
3.2. Resolving the Structure of Be$_{12}$Ti

Figure 3.2: Simulated X-ray diffraction patterns of pure beryllium, Be$_{17}$Ti$_2$, hexagonal Be$_{12}$Ti, and tetragonal Be$_{12}$Ti. X-ray wavelength used corresponds to Cu K-alpha source (1.5406 Å).

and hexagonal pseudo-cell, with all major peaks present in both materials occurring at similar $2\theta$ and with similar relative intensity. Some discrepancy does occur between minor peaks, and notably large reflections at 24, 34, 42, and 51 $2\theta$ are split in the tetragonal structure but not in the hexagonal structure. Interestingly there are broad similarities between both Be$_{12}$Ti patterns and Be$_{17}$Ti$_2$, although there are several differences. In particular the peak at 18 $2\theta$ in both Be$_{12}$Ti structures is not present in the Be$_{17}$Ti$_2$ pattern. Nonetheless, it is clear that there is a strong correspondence between the Be$_{17}$Ti$_2$ and Be$_{12}$Ti structures. This lends credence to the assertion by Gillam et al. that the work of Raeuchle and Rundle may have been performed on Be$_{17}$Ti$_2$ [182].

3.2.1 Density Functional Theory Simulations

To establish if the tetragonal phase is the stable phase at low temperature for Be$_{12}$Ti and can be used for further simulation study, DFT simulations of the tetragonal cell
3.2. Resolving the Structure of Be$_{12}$Ti

and hexagonal cell identified by Raeuchle and Rundle have been performed. All simulations were carried out using the CASTEP code [136, 137] parameterised as described in sections 2.1 and 2.2.

The classical ground state energy of each structure was calculated by geometry optimising the unit cells of each structure, and comparing the energy of the resulting phases to that of their metallic reference states (treated in the same way), as in equation 3.1:

$$E_f(\text{Be}_{12}\text{Ti}) = E_{\text{DFT}}(\text{Be}_{12}\text{Ti}) - E_{\text{DFT}}(\text{Ti}) - 12E_{\text{DFT}}(\text{Be})$$

The formation enthalpy of the hexagonal and tetragonal phases were -6.82 and -7.90 eV/formula unit respectively. This corresponds to a unit cell of the tetragonal phase having formation enthalpy 1.12 eV lower than the hexagonal phase. Such a large difference in the formation enthalpy strongly indicates that the tetragonal structure is the stable phase at low temperatures. At higher temperatures, the vibrational entropy/free energy of the system must also be taken into consideration, as this may reverse the stability of the two structures. This is calculated using the harmonic and quasiharmonic approximations as outlined in chapter 2.

Phonon dispersion curves and density of states were computed using the supercell method [78]. For completeness, these simulations were repeated with 2×2×2 and 3×3×2 supercells of both structures, corresponding to 234 and 312 atoms respectively. The simulated phonon dispersion curves and corresponding density of states are presented in figures 3.3 and 3.4 for the hexagonal and tetragonal structures respectively.
3.2. Resolving the Structure of Be$_{12}$Ti

Figure 3.3: Simulated phonon band structure and density of states of hexagonal Be$_{12}$Ti. Image courtesy of P. Burr.
3.2. Resolving the Structure of Be$_{12}$Ti

The dispersion curves for the tetragonal structure shows only positive (real) phonon modes indicating that it is mechanically stable. The hexagonal dispersion curves shows a negative or "soft" phonon mode at the M-point indicating that it is mechanically unstable. This negative phonon mode corresponds to a displacement of Ti in the [0001] direction. As the c displacement of the Ti atom is the primary difference between the hexagonal and tetragonal phases, this provides further evidence that the tetragonal
3.2. Resolving the Structure of Be$_{12}$Ti

phase is more stable at temperatures of interest.

In addition, integration of the phonon DOS was used to calculate the zero-point energy and constant volume vibrational contributions to the Helmholtz free energy ($F$). The quasiharmonic approximation (as described in section 2.2.2) was applied to find the same contributions, at constant pressure, to the Gibbs free energy. The Be$_{12}$Ti structure is an ideal structure to perform this analysis on, as the vibrational contributions to quantities such as heat capacity dominates below the Debye temperature, which for pure beryllium is unusually high at 1440 K [183] (only 110 K below the melting temperature) owing to its high stiffness and low atomic mass. As Be$_{12}$Ti is composed of mostly beryllium, it is reasonable to assume that it will have a similarly high Debye temperature. Gibbs and Helmholtz free energies calculated for each structure are shown in figure 3.5.

At temperatures up to 1550 K, which is the melting point of the pure Be reference state, all calculations indicate the total energy of the tetragonal structure is approximately 6 eV per formula unit lower than the hexagonal structure, strongly indicating that it is the equilibrium structure. Given that calculations based on both the harmonic and quasiharmonic approximation, for all cell sizes, point to the same conclusion, this provides strong evidence that the conclusion is robust.

3.2.2 Calculated Material Properties of Be$_{12}$Ti

Having shown that the tetragonal phase is the equilibrium phase at relevant temperatures, the harmonic and quasiharmonic approximation are now used to predict some fusion relevant materials properties of this phase. The thermal expansion and the bulk modulus of the tetragonal phase were calculated by fitting the Birch-Murnaghan equation-
3.2. Resolving the Structure of Be$_{12}$Ti

Figure 3.5: Simulated internal and Helmholtz free energy of formation for the tetragonal and hexagonal sub-cell of Be$_{12}$Ti as a function of temperature, as calculated by the harmonic and quasiharmonic (QH) approximations. Harmonic and quasiharmonic results appear so close as to be indistinguishable.

The volumetric thermal expansion is important for assessing the compatibility of structural materials subject to thermal cycling, as in a fusion environment. The predicted volumetric thermal expansion is in good qualitative agreement with the available experimental data, although it is approximately 3 to 5% lower. The predicted value of the bulk modulus at 273 K is 121.0 GPa, in close agreement with the experimental value (117.0 GPA [186]). In addition, at 0K it has previously been calculated using
3.2. Resolving the Structure of Be$_{12}$Ti

Figure 3.6: Thermodynamic data from quasi-harmonic calculations at 50K intervals. Dotted lines are fitted Birch-Murnaghan equations of state, and the crosses represent the minima of those curves. Image courtesy of P. Burr.

Figure 3.7: Volumetric thermal expansion coefficient ($\alpha_v$) and bulk modulus ($K_0$) of tetragonal Be$_{12}$Ti, predicted within the quasi-harmonic approximation, and comparison to experimental data for $\alpha_v$ [82].
DFT to be 120.5 GPa (3 GPa less than the predicted value), although this data was produced assuming the (incorrect) hexagonal pseudo-cell [95].

Further predicted properties, including elastic constants and lattice parameters are reported in table 3.1. Comparing the room temperature quasiharmonic and experimental lattice parameters, the quasiharmonic approximation overpredicts both the \( c \) and \( a \) parameters by around 2% which is typical of DFT simulations with the PBE exchange functional [187].

Table 3.1: Simulated lattice parameters and elastic data of tetragonal Be\(_{12}\)Ti with comparison to experimental data. For the ground state simulations, shear (\( G \)) and bulk (\( K \)) moduli were obtained from the stiffness constants (\( c_{ij} \)) using the Hill averaging method [188].

<table>
<thead>
<tr>
<th></th>
<th>( a ) (Å)</th>
<th>( c ) (Å)</th>
<th>( c_{11} ) (GPa)</th>
<th>( c_{12} ) (GPa)</th>
<th>( c_{13} ) (GPa)</th>
<th>( c_{33} ) (GPa)</th>
<th>( c_{44} ) (GPa)</th>
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</tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>123.6</td>
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<td>-</td>
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<tr>
<td>exp. (T=298K)</td>
<td>7.35(^a)</td>
<td>4.19(^a)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>117.0(^b)</td>
</tr>
</tbody>
</table>

\(^a\) [89] \(^b\) [186]

3.3 Inelastic Neutron Scattering in Beryllides

In addition to Be\(_{12}\)Ti, Be\(_{12}\)V is another candidate material that has been explored for fusion applications [82], while other Be\(_{12}M\) and Be\(_{13}M\) structures (i.e. Be\(_{12}\)W and Be\(_{13}\)Zr) have been considered based on their beryllium content [56]. Until recently, many of these compounds have not had any practical applications, thus there is a lack of available experimental data. Further, owing to the low atomic mass of beryllium, experimental techniques relying on charge density, (e.g. XRD and electron microscopy),
3.3. Inelastic Neutron Scattering in Beryllides

may be less effective in these materials. Conversely, inelastic neutron scattering is ideally suited to these materials, and can probe information both about the crystal structure and dynamic response of the lattice [183]. This makes it a good point of comparison for both DFT simulations and future experimental studies.

As such, following theoretical investigation of the Be\textsubscript{12}Ti structure, further investigations of other beryllides were undertaken for comparison with experimental neutron scattering data, in order to further validate the DFT model.

### 3.3.1 Theoretical Investigations

Six structures were investigated: Be\textsubscript{12}Ti, Be\textsubscript{12}Nb, Be\textsubscript{12}V, Be\textsubscript{12}Mo, Be\textsubscript{12}Ta, and Be\textsubscript{13}Zr. All of the Be\textsubscript{12}M compounds are isostructural with the Be\textsubscript{12}Ti tetragonal phase, while Be\textsubscript{13}Zr has a complex cubic structure of Fm\overline{3}c(226) symmetry [189] containing 8 formula units, as presented in figure 3.8. The structure contains one unique Zr site at \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\) and two Be sites at (0,0,0) and (0, 0.112, 0.178). Geometry optimisation of all structures was performed through DFT simulations in order to predict basic properties such as lattice parameters, which are compared to experimental values in table 3.2. Predicted values of the lattice parameters correspond closely to the experimental data, typically underestimating values by 1–2\%. Special positions of the Be sites in the Be\textsubscript{12}M structure also compare favourably to experimental data where available.

In order to gain more detailed information about the vibrational states of these materials for comparison with inelastic neutron scattering data, finite displacement calculations with the supercell method were used to calculate phonon DOS. 2\times 2\times 2 supercells were used for the Be\textsubscript{12}M structures. The choice of this supercell size is further validated by the close agreement of data calculated using the 52 and 312 atom cell shown in figure 3.5 for Be\textsubscript{12}Ti. On this basis, for the Be\textsubscript{13}Zr structure, which has 108 atoms
Table 3.2: Experimental and predicted lattice properties of Beryllides.

<table>
<thead>
<tr>
<th>property</th>
<th>Be$_{12}$V</th>
<th>Be$_{12}$Ti</th>
<th>Be$_{12}$Ta</th>
<th>Be$_{12}$Nb</th>
<th>Be$_{12}$Mo</th>
<th>Be$_{13}$Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>Exp.</td>
<td>DFT</td>
<td>Exp.</td>
<td>DFT</td>
<td>Exp.</td>
<td>DFT</td>
</tr>
<tr>
<td></td>
<td>7.266$^a$</td>
<td>7.240</td>
<td>7.35$^c$</td>
<td>7.361</td>
<td>7.334$^b$</td>
<td>7.309</td>
</tr>
<tr>
<td></td>
<td>7.278$^b$</td>
<td></td>
<td></td>
<td></td>
<td>7.329$^c$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.212$^b$</td>
<td></td>
<td></td>
<td></td>
<td>4.256$^c$</td>
<td></td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>221.4$^a$</td>
<td>218.5</td>
<td>226.4$^c$</td>
<td>225.6</td>
<td>229.5$^b$</td>
<td>224.6</td>
</tr>
<tr>
<td></td>
<td>223.1$^b$</td>
<td></td>
<td></td>
<td></td>
<td>228.6$^c$</td>
<td></td>
</tr>
<tr>
<td>x, Be2</td>
<td>0.361$^a$</td>
<td>0.349</td>
<td>-</td>
<td>0.350</td>
<td>-</td>
<td>0.352</td>
</tr>
<tr>
<td>x, Be3</td>
<td>0.277$^a$</td>
<td>0.288</td>
<td>-</td>
<td>0.281</td>
<td>-</td>
<td>0.283</td>
</tr>
</tbody>
</table>

3.3. Inelastic Neutron Scattering in Beryllides

Figure 3.8: Crystal structure of cubic Fm$\bar{3}$c(226) Be$_{13}$Zr with drop shadows to highlight atomic positions [189]. Zirconium sites are blue and beryllium sites green.

in the unit cell, a $1\times1\times2$ supercell was deemed sufficient. The simulated phonon DOS for all materials are presented in figure 3.9.

Materials with the Be$_{12}M$ structure all have similar phonon DOS (figure 3.9) as would be expected for materials with the same structure and similar chemistry. In all cases, no peaks are present until between 15-25 meV, where a singlet or doublet is present. The energy of these first peaks appears to correlate roughly to the atomic mass of the transition metal, occurring at approximately 24 and 27 meV for titanium and vanadium (48 and 51 u), 18 and 20 meV for niobium and molybdenum (93 and 96 u) and 15 meV for tantalum (181 u). This correlation is not complete, as the relative positions of the titanium and vanadium peaks are not in the order expected based on their mass, however they are so close in mass that it is possible other effects are dominant. Beyond
these first peaks, these materials show other broad similarities in profile, although these are difficult to quantify. The lowest energy phonon peaks in Be$_{13}$Zr conform with the described trend in atomic mass (zirconium 91 u), with a doublet occurring at around 22 meV. However, the DOS also contains two high intensity peaks at 79 and 91 meV, contrary to the Be$_{12}M$ structures.

3.3.2 Neutron Scattering

As mentioned previously, neutron scattering data can provide useful information about the elastic properties and structure of a material. In addition, it can lead to useful validation of DFT data. Thus, having calculated the phonon density of states for these materials, inelastic neutron scattering data is presented for comparison.

Samples

Six samples weighing approximately 5g were provided by C. Dorn of Materion Brush Inc., the details of which are presented in table 3.3. Samples were prepared through single stage synthesis in an induction furnace (i.e. elemental powders have been blended and consolidated before being melted to form the compounds). The samples were consolidated without a binder and heated to 1400°C in a BeO crucible for a minimum of one hour. Preliminary characterisation of the samples was carried out using XRD. Unfortunately this was hampered significantly by the form of the samples, some of which were too large to fit in the sample holder. Smaller samples could not be made due to the lack of appropriate facilities to process the beryllium containing samples (given that the dust poses an inhalation hazard). As such, it was not possible to polish the samples to achieve a flat surface, nor break the samples to an appropriate size to fit in the XRD instrument. Consequently, XRD analysis could not be performed on
Figure 3.9: Simulated phonon density of states for beryllide samples, normalised to highest intensity peak.
3.3. Inelastic Neutron Scattering in Beryllides

Be$_{12}$Nb and Be$_{12}$Mo samples. This was particularly problematic for the Be$_{12}$Mo sample, as it contained a large component of a second phase, which may have originated from the BeO crucible in which it was synthesised, however without XRD analysis this could not be verified.

Table 3.3: Samples investigated by neutron scattering with mass and preliminary characterisation technique.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (g)</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be$_{12}$Ti</td>
<td>4.57</td>
<td>Yes</td>
</tr>
<tr>
<td>Be$_{12}$V</td>
<td>4.71</td>
<td>Yes</td>
</tr>
<tr>
<td>Be$_{12}$Mo</td>
<td>4.76</td>
<td>No</td>
</tr>
<tr>
<td>Be$_{12}$Ta</td>
<td>5.33</td>
<td>Yes</td>
</tr>
<tr>
<td>Be$_{12}$Nb</td>
<td>6.19</td>
<td>No</td>
</tr>
<tr>
<td>Be$_{13}$Zr</td>
<td>5.20</td>
<td>Yes</td>
</tr>
</tbody>
</table>

XRD analysis of the samples (where possible) were consistent with the stated compositions and structures. In all cases, small secondary XRD patterns were observed which appear to be BeO, as would be expected owing to oxidisation of sample surfaces and preparation in BeO crucibles. The Be$_{13}$Zr sample also showed peaks attributed to pure Be, suggesting it was synthesised with excess beryllium, and thus zirconium rich Be$_{17}$Zr$_2$ was not present. It should be noted that the absence of beryllium peaks in other samples does not preclude its existence as a second phase, as pure beryllium is almost entirely X-ray transparent (and indeed is used as an X-ray window [64]) and thus would not be expected to produce a strong signal.

Experimental Details

Experimental results were gathered using the TAIPAN triple-axis neutron spectrometer, the general set-up of which is outlined in section 2.5. Two monochromators were considered, a graphite (002) monochromator with energy range 6-70 meV, and a copper monochromator with range 14-100 meV. Preliminary investigations showed the
graphite option to be more suitable as the 6-70 meV range contains ample information about the phonon response of these materials. In particular, the 6-20 meV range was found to include second order scattering contributions which, after further analysis, proved to be useful (see subsection 3.3.3). In addition, given that this technique is intensity limited and by extension time consuming, given the limited beam-time, it was decided that the lengthy commissioning process of the copper monochromator would have too greatly restricted the time over which experiments could be performed.

The graphite monochromator was used with continuous vertical and horizontal focusing, a sapphire high energy filter and no collimators (to increase signal). Samples were mounted in a custom rectangular aluminium frame, and held in place with aluminium foil (see figure 3.10). This set-up was shown not to contribute significantly to the background counts, has very low activation in the neutron beam and simplified working with the beryllide samples (through hazard reduction) by fully encapsulating them. To further reduce scatter from the sample holder, a mask of cadmium (which is a strong neutron absorber) was applied. The setup of the sample and sample holder is shown in figure 3.10.

Initial data collection was performed at 2 K with a cryofurnace, and 286 K without, as presented for Be$_{12}$Ti in figure 3.11. Comparison of the two data sets shows that there is no tangible benefit from using the cryofurnace, with no increase in resolution but a decrease in signal. Given that use of the cryofurnace significantly increased the duration of the experiments, due to the time required for samples to reach temperature, its use was discontinued in subsequent runs.

Data was collected over the full available energy range (8-70 meV) in increments of 0.2 meV with a collection time of 50 s. As the experiment proceeded, it became clear that analysis of second order scattering in the 8-20 meV range could provide increased
3.3. Inelastic Neutron Scattering in Beryllides

Figure 3.10: Left: sample in holder. Sample is secured in an aluminium frame with aluminium foil, and frame shielded with cadmium. Right: sample setup within the TAIPAN instrument.

Figure 3.11: Data collected at 2 K with the cryofurnace setup and at 295 K.
energy resolution and signal to noise ratio, which are degraded as a consequence of broadening effects at higher energies. As such, scans were repeated in this region with a step size of 0.1 meV and collection time of 100s (where possible).

### 3.3.3 Data and Analysis

Figure 3.12 shows the final collected data, normalised by monitor counts and by maximum intensity. It is clear there are significant differences between the experimental data and the theoretical data (presented in figure 3.9). The experimental data shows no sharp peaks, which are predicted in the theoretical data, instead appearing as broad humps with what appears to be noise superimposed. Secondly, the intensity of the experimental data appears to increase with increasing incident energy. Thirdly, the sharpest peaks in the experimental data appear below 20 meV, where no peaks are predicted in the DFT simulations.

In analysing these differences, it is necessary to deconvolute experimental effects from the true phonon DOS. Firstly, the effect of instrument broadening must be taken into consideration. There are two known experimental sources of broadening. The incident neutron beam is not entirely monochromatic, rather it can be described as a Gaussian distribution with Full-Width-Half-Maximum (FWHM) of 1.1 meV. This is independent of the energy, E. Another source of broadening is associated with the monochromator, which causes energy dependent broadening. This was characterised for the Taipan instrument [173] using the Raytracing modelling of Stampfl and Bertinshaw [193] who derived equation 3.2 to describe the broadening effect.

\[
\text{FWHM} = 1.59 \times 10^{-7}E^4 - 3.57 \times 10^{-5}E^3 + 3.24 \times 10^{-3}E^2 + 1.53 \times 10^{-2}E \quad (3.2)
\]

Based on this equation, the broadening is expected to increase from a minimum FWHM
Figure 3.12: Detector and maximum intensity normalised neutron scattering data for six Beryllides, $\text{Be}_{12}M$, $M=\text{Ti}, \text{V}, \text{Nb}, \text{Mo}, \text{Ta}$ and $\text{Be}_{13}\text{Zr}$. 
of 0.6 meV at an energy of 8 meV to a maximum of 8.0 meV at 70 meV. This is visualised with the incident neutron energy broadening in figure 3.13. The variable broadening from the monochromator also explains why the intensity of the experimental data increases at higher energy, since for a given peak intensity, a larger FWHM corresponds to a greater total area under the peak.

It is impossible to deconvolute the effect of broadening from the experimental data, however it is possible to apply it to the DFT data. The effects of the two contributions to broadening are applied to the DFT data in order that it may be compared to the experimental data. This is shown in figure 3.14 for Be$_{12}$Ti.

When broadening is applied, the DFT data begins to more closely resemble the experimental data, although it does nothing to address the discrepancy in the 8-20 meV region. In particular, the overall increase in peak intensity with energy is replicated even with only the filter broadening, while the addition of variable broadening seems to overestimate this effect. Indeed, the addition of monochromator broadening appears
3.3. Inelastic Neutron Scattering in Beryllides

Figure 3.14: Simulated broadening of DFT predicted DOS results for Be$_{12}$Ti with comparison to experimental results. a) predicted phonon DOS, b) phonon DOS broadened with FWHM from the monochromator only, c) phonon DOS broadened with FWHM from the filter only, d) phonon DOS broadened with both contributions and e) experimental results.

to make the DFT data more poorly resolved than the experimental data, suggesting that its effect has been significantly overestimated.

In order to more accurately characterise the instrument broadening, a broadening term was fitted to the DFT data. In this scheme, two models of broadening were considered: a constant FWHM similar to the effect of the filter and an linear energy dependent term, FWHM = a+Eb (where a and b are constants), approximating the effect of both the filter and monochromator. To achieve this, the experimental data was area normalised for comparison. The FWHM maximum was applied to the DFT data, which was also area normalised, and the least squares (absolute difference) between the two data sets taken in the 24-20 meV range. The FWHM (or the a and b constants for the
energy dependent model) was then iteratively altered to minimise the sum of the least squares. While this approach did effectively minimise the absolute difference between the DFT and experimental data, in all cases it resulted in significant over-broadening of the DFT data, and thus is not useful for further analysis. This does, however, suggest that there are other reasons for the differences between the DFT and experimental data apart from the instrument broadening.

The broadening effect does not explain the presence of peaks in the 8-20 meV range in the experimental data, which are not predicted in the DFT data. This puzzle can be resolved by noticing that the reflections in this region bear striking similarity to the spectrum in the 32-80 meV region, compressed by a factor of 4 in the energy axis. This suggests the low energy peaks may be attributed to the effects of second and third order scattering, 4 and 9 times reduced from the energy of the fundamental modes. To examine this possibility, figure 3.15 shows second and third order reflections of the DFT predicted spectrum, as well as the experimental spectrum. For further confirmation, enhanced resolution experimental data in the 8-20 meV range has been extrapolated to the 32-80 meV, the range corresponding to the fundamental assuming that the 8-20 meV range is the second order reflection (see left hand side of figure 3.15).

Figure 3.15 shows that the third order reflection of the DFT and experimental data is only significant below 10 meV and thus can be discounted from further analysis. Further, peaks in the experimental data in the 8-20 meV range correspond very closely with the fundamental reflections in the 32-80 meV range, compressed in the energy axis by a factor of 4. Thus, the hypothesis that the experimental peaks below 20 meV are a consequence of second order rather than first or third order reflections is consistent with experiment, and helps explain the apparent discrepancy between DFT and experimental data. Further, it appears that much better energy resolution is achieved in the second order reflection in comparison to the first order reflection (presumably
3.3. Inelastic Neutron Scattering in Beryllides

Figure 3.15: Left: experimental neutron scattering data, with data in the 8-24 meV region (assumed to be second order reflections) extrapolated and normalised by monitor counts (CN) and originating monitor counts (OCN). Right: simulated phonon density of states with simulated higher order reflections.

due to the much smaller contribution from monochromator broadening).

To modify DFT data to include the second order reflection, it must be scaled in line with the experimental data. The magnitude of this scaling, however, is difficult to establish. The simplest option is to scale by the average intensity of the second order experimental data (8-18 meV) relative to the first order reflection (32-72 meV), which suggests that the second order reflection would have a constant scaling factor of 0.66 relative to the fundamental.

When extrapolating second order experimental data to generate a second data set, it is unclear whether to scale the data by the monitor counts in the 8–20 meV region, or, assuming the data is primarily the result of higher order reflections, from the originating monitor counts (in the 32–80 meV region). In either case the data is qualitatively very similar with all major peaks present in both data sets.
3.3.4 Comparison

Having examined the causes of discrepancy between DFT and experimental data, a comparison can now be made. Presented in figures 3.16 and 3.17 is experimental data (count and intensity normalised) and the normalised simulated phonon DOS for all samples. Given the increased resolution of second order reflections in the experimental data, the extrapolated second order data (originating count normalised and intensity normalised) is also presented, as are second order reflections from the phonon DOS (scaled by a factor of 0.66).

For all materials, it appears that the enhanced second order reflection is less broadened and consequently has better energy resolution than the fundamental. Further there is a strong correspondence between the extrapolated 8-20 meV data and the fundamental, again consistent with the former being primarily composed of contributions from the second order terms.

Given the better energy resolution of the extrapolated second order experimental data, it is perhaps the best point of comparison for the DFT data. It can be seen that broadly, there is a strong correspondence between the shape of the two data sets. Many peaks do, however, seem significantly shifted between the experimental and DFT data, for example the $\text{Be}_{12}\text{Nb}$ DFT peak at 37 meV appears at around 35 eV in the experimental data. This underlines that DFT phonon DOS is a prediction and may not perfectly reflect the real material. In particular, the phonon DOS is determined both by the crystal structure and the energy landscape about the equilibrium atomic positions. From table 3.2, DFT simulations typically under predict lattice parameters by 1–2%, which would similarly shift peak positions in the phonon DOS.

While the general shape of the experimental data corroborates the DFT data, the
Figure 3.16: Comparison of simulated phonon DOS and count normalised neutron scattering data for Be$_{12}$Ti (red), Be$_{12}$V (orange) and Be$_{12}$Mo (yellow). Simulated phonon DOS 2nd harmonic spectrum is shown in grey (low energy, top) superimposed on the predicted DOS, as is the extrapolated experimental 2nd harmonic (high energy, bottom) superimposed on the experimental data.
3.3. *Inelastic Neutron Scattering in Beryllides*

Figure 3.17: Comparison of simulated phonon DOS and count normalised neutron scattering data for \( \text{Be}_{12}\text{Nb} \) (light green), \( \text{Be}_{12}\text{Ta} \) (dark green) and \( \text{Be}_{13}\text{Zr} \) (purple). Simulated phonon DOS 2nd harmonic spectrum is shown in grey (low energy, top) superimposed on the predicted DOS, as is the extrapolated experimental 2nd harmonic (high energy, bottom) superimposed on the experimental data.
3.4 Summary and Conclusions

The crystal structure of Be$_{12}$Ti has been confirmed as exhibiting the tetragonal/ I$_4$/mmm symmetry rather than hexagonal/P$_c$/mmm symmetry at low temperature using the harmonic and quasiharmonic approximations. Further, given the large energy difference between the two phases over all temperatures investigated, this conclusion is also likely to hold true at elevated temperatures. The source of confusion between the two phases is explained through the close relation of the phases, as well as the presence of the hexagonal Be$_{17}$Ti$_2$ phase, which shows strong similarities in the simulated diffraction pattern. Some basic fusion relevant properties of Be$_{12}$Ti have also been predicted as a function of temperature, including the bulk modulus, thermal expansivity and heat capacity.

Phonon density of states have been simulated for Be$_{12}$Ti, Be$_{12}$V, Be$_{12}$Ta, Be$_{12}$Nb and Be$_{13}$Zr using DFT, and compared to inelastic neutron scattering data. It was found that performing scattering experiments at room temperature was sufficient, without the use of a cryo furnace. Broadening of the neutron scattering data occurred from two sources; the filter and monochromator, although the latter proved to be less significant than suggested by prior modelling [193]. Nonetheless, the data is so broadened that direct quantitative comparison to the DFT data is difficult. It was found that enhanced energy resolution could be achieved by examining the second order reflections of the experimental data is so broadened that it is difficult to make conclusions beyond this. In particular, the reasons for the shifting of certain peaks between the two data sets cannot be identified with certainty. As such, while the experimental data can be qualitatively used to qualify the DFT data, meaningful quantitative comparison is difficult.
experimental data. These are at lower energy than the fundamental and thus were less
broadened, and, given the absence of peaks in the \(<20\) meV DFT data can be easily
deconvoluted from the fundamental reflection.

Qualitative comparison between DFT and experimental data shows good agreement,
with the broadened DFT data having similar shape and peak positions to the experi-
mental data. Some peaks do, however, appear shifted by up to 3 meV between the two.
This may be explained as an artefact of the broadening inherent in the experimental
data, or due to differences in the energy surface or lattice parameters predicted by
DFT simulation, the latter of which may differ from experimental values by up to 2%.

3.5 Contributions

Inelastic neutron scattering experiments were performed using the TAIPAN facility
as part of the TAIPAN grant 5338. The experiments and analysis were conducted in
collaboration with P. A. Burr, A. P. J. Stampfl and E.G. Obbard. Analysis of QH
simulations in Be\textsubscript{12}Ti was also conducted in conjunction with P. A. Burr. Beryllide
samples were provided by C. K. Dorn of Materion Brush. Preliminary sample char-
acterisations were performed using facilities provided by the University of New South
Wales. Computing resources were provided by Imperial College London high perform-
ance computing service.
Chapter 4

Defects in Be$_{12}M$ Beryllides

This work is published in:
M. L. Jackson, P. A. Burr, R. W. Grimes “Defect processes in Be$_{12}X$ (X = Ti, Mo, V, W)”, Nuclear Fusion, 57, 8 (2017) [194]

4.1 Introduction

As discussed in chapters 1 and 3, the Be$_{12}M$ beryllides have been suggested for use as neutron multipliers and first wall materials in future fusion reactors [56]. Indeed it is expected that one of the TBM designs tested in Iter will use Be$_{12}$Ti [195]. Having investigated the basic properties of a wide range of beryllides in chapter 3, the focus here is on the four most likely for use as neutron multipliers, as identified by Yamada et al [56]. These are Be$_{12}$Ti, Be$_{12}$V, Be$_{12}$Mo and Be$_{12}$W. Of these, Be$_{12}$V and Be$_{12}$Ti have been identified as leading candidates as they have better neutronic properties than Be$_{12}$Mo and Be$_{12}$W. While Be$_{12}$Ti and Be$_{12}$V have very similar fusion relevant thermo-physical properties, Be$_{12}$Ti is significantly easier to fabricate [196], and thus is considered most likely for fusion applications.
Table 4.1: Fusion relevant materials properties of Be$_{12}$Ti, Be$_{12}$V and beryllium. Reproduced from [82].

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Be$_{12}$Ti</th>
<th>Be$_{12}$V</th>
<th>Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$ (°C)</td>
<td>1600</td>
<td>1700</td>
<td>1283</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2.26</td>
<td>2.37</td>
<td>1.85</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>280</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>1260°C:30-90</td>
<td>20°C:140</td>
<td>20°C:580</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>-</td>
<td>-</td>
<td>1530</td>
</tr>
<tr>
<td>Thermal expansion coefficient (10$^{-6}$/K)</td>
<td>100°C:13.2</td>
<td>100°C:14.5</td>
<td>100°C: 11.5</td>
</tr>
<tr>
<td>Thermal conductivity (W/m/K)</td>
<td>100°C: 41</td>
<td>100°C: 38</td>
<td></td>
</tr>
<tr>
<td>Microhardness (GPa)</td>
<td>10</td>
<td>11</td>
<td>2.25</td>
</tr>
<tr>
<td>DBTT (°C)</td>
<td>860</td>
<td>790</td>
<td>-</td>
</tr>
<tr>
<td>Fracture toughness (MPa$^{0.5}$)</td>
<td>-</td>
<td>20°C: 0.8</td>
<td>20°C: 9.8</td>
</tr>
</tbody>
</table>

Many experimental investigations of the basic properties of Be$_{12}$Ti and Be$_{12}$V have been undertaken, with the result that such properties are well characterised [186, 82, 197]. An overview of the two materials is shown in table 4.1 [82]. Further, the effect of neutron irradiation on the microstructure of Be$_{12}$Ti has been investigated, although as previously noted it is not possible to replicate the fusion neutron flux profile. Kurinskiy et al. [178] investigated irradiation effects in Be$_{12}$Ti between 740 and 873 K (which is approximately the operating temperature envisaged for a breeder blanket [178]), irradiating to a fluence of 8.07×10$^{25}$, which is significantly higher than other studies. At these temperatures, the dominant degradation effect appeared to be the formation of 15-20 nm He bubbles, leading to a swelling of 0.28%. This is significantly lower than for pure beryllium [198], but is not insignificant, and further is expected to be more prevalent under a fusion neutron flux where more transmutation of beryllium to helium would occur. Another important metric is the retention of tritium, which through ion implantation experiments followed by annealing, has been shown to be accommodated in the same bubbles with helium [199, 200]. Retention has also been shown to be much lower than in pure beryllium [178, 201, 93].
4.2. Point Defects

It is important to understand the formation of helium and tritium bubbles in Be$_{12}$Ti, given they are the source of swelling and tritium retention. It is likely that bubbles would be nucleated from smaller defects such as vacancies and vacancy clusters, thus to understand their formation it is necessary to investigate the point defect chemistry of the material. Surprisingly, no investigations of the intrinsic defect chemistry in Be$_{12}$Ti have been undertaken, although the accommodation of hydrogen at interstitial sites has been investigated using DFT simulations by Fujii et al [91], who found six stable interstitial sites with solution energies between 0.11 and 1.06 eV.

Allouche et al [96] investigated hydrogen accommodation in isostructural Be$_{12}$W, and, in addition to investigating accommodation interstitially also investigated accommodation in Be vacancies. Vacancy formation energies for the Be1, Be2, Be3 and W sites were calculated to be 1.38, 1.14, 1.48 and 3.25 eV respectively. It was also found that, as for pure Be [79], several hydrogen atoms can be accommodated in a single vacancy.

Beyond vacancy formation energies of Be$_{12}$W, no investigation of the intrinsic defect chemistry of any of the Be$_{12}M$ compounds has been made previously, despite an understanding of defect behaviour being so important for understanding the mechanisms dictating the radiation response of these materials. As such, this section presents a thorough investigation of point defects and small clusters in Be$_{12}$Ti, Be$_{12}$V, Be$_{12}$Mo and Be$_{12}$W.

4.2 Point Defects

During a radiation damage cascade in a material, two types of defect disorder may be formed: Frenkel disorder, where an atom is displaced from its lattice site to form a
4.2. Point Defects

vacancy and interstitial:

\[ \text{Be}_\text{Be} \rightarrow \text{V}_{\text{Be}} + \text{Be}_i \]  \hspace{1cm} (4.1)

or antisite disorder, where a displacement causes two species to swap sublattices:

\[ \text{Be}_\text{Be} + M_M \rightarrow M_{\text{Be}} + M_M \]  \hspace{1cm} (4.2)

Thus, for a material with two species such as Be\textsubscript{12}M, at a minimum V\textsubscript{Be}, V\textsubscript{M}, Be\textsubscript{i}, M\textsubscript{i}, Be\textsubscript{M} and M\textsubscript{Be} must be simulated to begin building a picture of the defect chemistry of the material. This is fairly simple for the antisite and vacancy species, however the interstitial sites in this structure have not previously been identified.

In this work, interstitial sites have been identified for the first time using a brute force approach. 1 \times 1 \times 2 supercells of Be\textsubscript{12}Ti was seeded with an equally spaced grid of 10 \times 10 \times 10 beryllium and titanium interstitials (in separate simulations) in a range between (000) and (\frac{1}{2} \frac{1}{2} \frac{1}{2}) of the unit cell, thus covering all symmetry distinct sites. The energy of each replica was then evaluated using DFT, following the methodology outlined in chapter 2 section 2.1. The 20 lowest energy symmetrically distinct replicas were then reproduced in a 2 \times 2 \times 2 supercell and geometry optimised.

For the beryllium interstitials, all replicas converged to three symmetrically distinct sites, while for the titanium interstitials four sites were identified, three of which are identical to the beryllium sites. These are shown in figure 4.1.
4.2. Point Defects

Figure 4.1: Left: intrinsic interstitial sites within the Be$_{12}$Ti structure. Right: coordination polyhedra of interstitial sites within the Be$_{12}$Ti structure.

Of the three sites that can accommodate both transition metals and beryllium, i1 is a site with 2b symmetry coordinated by four Be3 sites and two transition metal sites, i2 has 4b symmetry and is coordinated by 4 Be2 sites, i3 have 8h symmetry and is coordinated by one transition metal site, four Be3 sites, two Be2 sites and one Be1 sites. The i4 site is stable only for the transition metal interstitial, has 4c symmetry and is coordinated by six Be2 sites and two Be3 sites. There is significant perturbation of the Be2 sites when the transition metal is accommodated on the i4 site.

Having identified the position of the interstitial sites, the formation energies, $E_f$, of vacancies and interstitials were calculated. The formation energies of beryllium vacancies and interstitials are presented in table 4.2, with previous data for Be$_{12}$W and pure
Table 4.2: Defect formation enthalpy for Be interstitials and vacancies in Be$_{12}$M materials. Prior DFT data for Be$_{12}$W and pure beryllium is shown for comparison.

<table>
<thead>
<tr>
<th></th>
<th>Be$_{12}$V</th>
<th>Be$_{12}$Ti</th>
<th>Be$_{12}$Mo</th>
<th>Be$_{12}$W [202]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_{Be1}$</td>
<td>1.59</td>
<td>1.60</td>
<td>1.59</td>
<td>1.38</td>
</tr>
<tr>
<td>V$_{Be2}$</td>
<td>1.48</td>
<td>1.43</td>
<td>1.34</td>
<td>1.20</td>
</tr>
<tr>
<td>V$_{Be3}$</td>
<td>1.64</td>
<td>1.53</td>
<td>1.66</td>
<td>1.47</td>
</tr>
<tr>
<td>interstitials</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be$_{i1}$</td>
<td>2.95</td>
<td>3.19</td>
<td>3.54</td>
<td>3.81</td>
</tr>
<tr>
<td>Be$_{i2}$</td>
<td>2.03</td>
<td>1.86</td>
<td>2.37</td>
<td>2.50</td>
</tr>
<tr>
<td>Be$_{i3}$</td>
<td>3.54</td>
<td>3.69</td>
<td>3.92</td>
<td>4.14</td>
</tr>
</tbody>
</table>

beryllium shown for comparison.

For all materials, the lowest energy vacancy site is V$_{Be2}$. V$_{Be1}$ is the next lowest energy site followed by V$_{Be3}$ in all materials with the exception of Be$_{12}$Ti. The relative magnitude of the energy difference between sites for each material is low (compared to the formation energy), with a maximum difference of 0.32 eV for Be$_{12}$Mo. It is also notable that the energy of all V$_{Be}$ species is similar across all materials. This may be expected, as all Be sites are primarily coordinated by other beryllium sites rather than transition metal sites; thus the transition metal would likely not have a large influence on the energy of a vacancy. For the accommodation of beryllium interstitials, the i2 site has the lowest energy for all materials, followed by the i1 and i3 sites. The formation energy of Be$_{i2}$ varies significantly between materials, being the lowest in Be$_{12}$Ti (1.86 eV) and highest in Be$_{12}$W (2.50 eV).

Be$_{12}$W results are in excellent agreement with those by Allouche et al. giving a good degree of confidence in the methodology. By comparison to pure beryllium, beryllium vacancy formation is less energetically favourable in all Be$_{12}$M materials, while interstitial formation is significantly more energetically favourable.
4.2. Point Defects

Table 4.3: Defect formation enthalpies of transition metal vacancies and interstitials in Be$_{12}M$ compounds. DFT data from previous studies is shown for Be$_{12}$W for comparison.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Be$_{12}$V</th>
<th>Be$_{12}$Ti</th>
<th>Be$_{12}$Mo</th>
<th>Be$_{12}$W</th>
<th>Be$_{12}$W [202]</th>
</tr>
</thead>
<tbody>
<tr>
<td>vacancies</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_M$</td>
<td>3.37</td>
<td>4.10</td>
<td>3.61</td>
<td>3.16</td>
<td>3.25</td>
</tr>
<tr>
<td>interstitials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_{i1}$</td>
<td>4.81</td>
<td>5.37</td>
<td>7.26</td>
<td>8.11</td>
<td>-</td>
</tr>
<tr>
<td>$M_{i2}$</td>
<td>4.79</td>
<td>5.10</td>
<td>5.60</td>
<td>6.48</td>
<td>-</td>
</tr>
<tr>
<td>$M_{i3}$</td>
<td>5.59</td>
<td>7.47</td>
<td>8.80</td>
<td>10.11</td>
<td>-</td>
</tr>
<tr>
<td>$M_{i4}$</td>
<td>4.69</td>
<td>4.19</td>
<td>4.84</td>
<td>5.95</td>
<td>-</td>
</tr>
</tbody>
</table>

The formation energies of transition metal vacancies and interstitials are shown in table 4.3. The energy of formation for $V_M$ is lowest in Be$_{12}$W (3.16 eV) and highest in Be$_{12}$Ti (4.10 eV). The lowest energy interstitial site for all materials is the $i4$ site, with interstitial energies ranging from 4.19 eV in Be$_{12}$Ti to 5.95 eV in Be$_{12}$W. There is a noticeable difference in the transition metal interstitial energy between Be$_{12}$V/Ti and Be$_{12}$Mo/W, with it being significantly higher for the latter two materials for all sites.

Antisite formation energies are shown in table 4.4. Accommodation of beryllium on a transition metal site has a high, relatively consistent formation energy of 2.76-3.55 eV for all materials. This is likely due to the large size mismatch between Be and the transition metal species. The Be2 sites provide the lowest energy to accommodate a transition metal for all materials, with formation enthalpy of 0.99 and 0.95 eV for V$_{Be2}$ and Ti$_{Be2}$ respectively, although it is significantly higher for Mo$_{Be2}$ (1.56 eV) and in particular W$_{Be2}$ (3.81 eV). The Be2 site is the only site which is coordinated with only one transition metal site, rather than two as for the Be1 and Be3 sites, which is likely the reason for the lower formation energy.
Table 4.4: Formation energies of antisite defects in $\text{Be}_{12}M$ compounds.

<table>
<thead>
<tr>
<th>defect</th>
<th>$\text{Be}_{12}\text{V}$</th>
<th>$\text{Be}_{12}\text{Ti}$</th>
<th>$\text{Be}_{12}\text{Mo}$</th>
<th>$\text{Be}_{12}\text{W}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Be}_M$</td>
<td>2.83</td>
<td>3.55</td>
<td>3.09</td>
<td>2.76</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be}1}$</td>
<td>3.10</td>
<td>3.26</td>
<td>4.13</td>
<td>4.43</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be}2}$</td>
<td>0.99</td>
<td>0.95</td>
<td>1.56</td>
<td>3.81</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be}3}$</td>
<td>1.79</td>
<td>2.50</td>
<td>3.40</td>
<td>3.81</td>
</tr>
</tbody>
</table>

### 4.3 Defect disorder processes

As mentioned, when a material is exposed to radiation, defects are formed through radiation damage processes, namely Frenkel and Antisite disorder. As such, it is important to evaluate the overall energy of the defect process rather than only the isolated defect. In addition, at elevated temperatures (such as may be experienced during fabrication) an equilibrium concentration of defects will exist dependent on the energy of these defect processes. In addition to Frenkel and antisite disorder, Schottky disorder will also contribute to the defect population under such circumstances. In this process, vacancies are formed in a stoichiometric ratio:

$$12\text{Be}_{\text{Be}} + M_M \rightarrow 12\text{V}_{\text{Be}} + V_M + \text{Be}_{12}M$$ (4.3)

It should be noted however that exact stochiometry is only entirely enforced in ionic materials due to the need for charge balancing, and as such some other combinations of defects may be formed in metallic $\text{Be}_{12}M$ causing the material to deviate from stoichiometry (which will be examined in section 4.5). The energy per defect for defect disorder processes are shown in table 4.5. An energy range is produced for each process due to the range of formation energies for defects on different Be and interstitial sites. At equilibrium the lowest energy defect process are the most likely to occur. This is not the case, however, for radiation damage processes which are decidedly not equilibrium...
4.4. Defect Clusters

Table 4.5: Energy ranges for intrinsic defect processes in Be$_{12}M$ compounds based on defect formation energies presented in tables 4.2-4.4.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Be$_{12}$V</th>
<th>Be$_{12}$Ti</th>
<th>Be$_{12}$Mo</th>
<th>Be$_{12}$W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be Frenkel</td>
<td>1.76 - 2.59</td>
<td>1.64 2.65</td>
<td>1.85 2.79</td>
<td>1.85 - 2.81</td>
</tr>
<tr>
<td>M Frenkel</td>
<td>4.03 - 4.48</td>
<td>4.15 - 5.78</td>
<td>4.22 - 6.20</td>
<td>4.55 - 6.63</td>
</tr>
<tr>
<td>Schottky</td>
<td>1.63 - 1.77</td>
<td>1.63 - 1.79</td>
<td>1.51 - 1.81</td>
<td>1.35 - 1.60</td>
</tr>
<tr>
<td>Antisite</td>
<td>1.91 - 2.96</td>
<td>2.25 - 3.41</td>
<td>2.33 - 3.61</td>
<td>3.29 - 3.60</td>
</tr>
</tbody>
</table>

processes, thus higher energy processes may also be significant.

For all materials, Schottky disorder is the lowest energy defect process, and has the lowest energy in Be$_{12}$W (1.35 eV/defect). In Be$_{12}$V and Be$_{12}$Ti, beryllium Frenkel disorder has energy of 1.76 and 1.64 eV/defect respectively, which is only 0.14 and 0.01 eV/defect higher than for Schottky disorder. Antisite disorder may also be significant for Be$_{12}$V, being only 0.3 eV/defect higher than for Schottky disorder. In all other materials antisite and transition metal Frenkel disorder are very unfavourable due to the high formation energies of defects on the transition metal sublattice.

4.4 Defect Clusters

In addition to point defects, it is important to investigate small point defect clusters as these may provide the nucleation points for extended defects such as dislocation loops, voids and bubbles. Formation energy is not a particularly useful measure for clustering, as what is important is the relative energy of the bound and unbound defects. As such, it is more useful to quantify the binding energy, $E_B$, of the cluster, which is the energy of formation from two isolated defects. The simplest cluster would be of either two vacancies or interstitials:

$$V_{Be} + V_{Be} \rightarrow V_{Be} V_{Be} \quad (4.4)$$
Given that this structure has three beryllium sites, one metal site and four interstitial sites however, there are many different possible configurations of these defects, which may have significantly different formation enthalpies. Binding energies are calculated with respect to the lowest formation energy defects of that type (e.g. for a divacancy $V_{\text{Be}2}$). The binding energy of all symmetrically distinct nearest neighbour vacancy clusters, including $V_{\text{Be}}V_{\text{Be}}, V_{\text{Be}}V_M$ and $V_MV_M$ are shown in table 4.6.

For all materials, some orientations of $V_{\text{Be}}V_{\text{Be}}$ clusters have negative binding energy, suggesting formation of these clusters is favourable from the isolated vacancies. In particular, the $V_{\text{Be}2}V_{\text{Be}2}$ divacancy orientated out of the (001) plane is the most favourable for all materials, with binding energy from -0.21 in Be$_{12}$V to -0.02 eV in Be$_{12}$W. Further, in Be$_{12}$V there are several other favourable clusters, while in the other materials no other $V_{\text{Be}}V_{\text{Be}}$ cluster is favourable, although some only have very small positive binding energies.

All $V_MV_M$ clusters are strongly unfavourable, with binding energies in excess of 0.50 eV. This is likely due to the large size of the transition metal species, which would cause the formation of a divacancy to create large localised strains. Several $V_MV_{\text{Be}}$ clusters have negative binding energy and, notably, $V_MV_{\text{Be}2}$ has strongly negative binding energy in all materials, ranging from -0.54 to -0.19 eV in Be$_{12}$V and Be$_{12}$W respectively. Given that there are several favourable vacancy clusters, these may form nucleation points for voids and bubbles, although more work is needed to confirm this. It is also possible that the introduction of radiogenic hydrogen and helium may stabilise some vacancy clusters that have slight positive binding energy, although again further work would be needed to confirm this.
Table 4.6: Binding energies of beryllium and transition metal vacancies with respect to \( V_{Be2} \) and \( V_M \). Negative values mean binding is favourable and positive unfavourable. 

<table>
<thead>
<tr>
<th>di-vacancy</th>
<th>( Be_{12}V )</th>
<th>( Be_{12}Ti )</th>
<th>( Be_{12}Mo )</th>
<th>( Be_{12}W )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{Be3}V_{Be3} ) (in plane)</td>
<td>0.37</td>
<td>0.41</td>
<td>0.74</td>
<td>0.92</td>
</tr>
<tr>
<td>( V_{Be3}V_{Be3} ) (out of plane)</td>
<td>0.37</td>
<td>0.44</td>
<td>0.35</td>
<td>0.74</td>
</tr>
<tr>
<td>( V_{Be2}V_{Be3} ) (in plane)</td>
<td>0.04</td>
<td>0.30</td>
<td>0.70</td>
<td>0.46</td>
</tr>
<tr>
<td>( V_{Be2}V_{Be3} ) (out of plane)</td>
<td>-0.08</td>
<td>0.04</td>
<td>0.12</td>
<td>0.19</td>
</tr>
<tr>
<td>( V_{Be2}V_{Be2} ) (in plane)</td>
<td>-0.01</td>
<td>0.22</td>
<td>0.03</td>
<td>0.11</td>
</tr>
<tr>
<td>( V_{Be2}V_{Be2} ) (in plane 2)</td>
<td>-0.08</td>
<td>0.35</td>
<td>0.12</td>
<td>0.22</td>
</tr>
<tr>
<td>( V_{Be2}V_{Be2} ) (out of plane)</td>
<td>-0.21</td>
<td>-0.04</td>
<td>-0.09</td>
<td>-0.02</td>
</tr>
<tr>
<td>( V_{Be1}V_{Be2} )</td>
<td>-0.04</td>
<td>0.26</td>
<td>0.25</td>
<td>0.33</td>
</tr>
<tr>
<td>( V_{Be1}V_{Be1} )</td>
<td>0.23</td>
<td>0.38</td>
<td>0.56</td>
<td>0.65</td>
</tr>
<tr>
<td>( V_{Be1}V_{Be3} )</td>
<td>0.16</td>
<td>0.63</td>
<td>0.46</td>
<td>0.52</td>
</tr>
<tr>
<td>( V_MV_M )</td>
<td>0.75</td>
<td>0.50</td>
<td>0.58</td>
<td>0.72</td>
</tr>
<tr>
<td>( V_MV_{Be3} )</td>
<td>-0.04</td>
<td>-0.04</td>
<td>0.17</td>
<td>0.22</td>
</tr>
<tr>
<td>( V_MV_{Be2} )</td>
<td>-0.54</td>
<td>-0.41</td>
<td>-0.29</td>
<td>-0.19</td>
</tr>
<tr>
<td>( V_MV_{Be1} )</td>
<td>0.04</td>
<td>-0.02</td>
<td>0.37</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Binding energy of beryllium di-interstitials is shown in table 4.7. Energies of transition metal di-interstitials were not calculated as preliminary investigations revealed extremely high positive binding energies (in excess of 10 eV) and thus they are unlikely to be relevant to the defect chemistry of the material. For all materials, the cluster with the lowest binding energy is \( Be_{Be4} \) (i.e. the accommodation of two Be atoms on a single i4 site). Indeed for \( Be_{12}V \) and \( Be_{12}Ti \), this cluster is energetically favourable with binding enthalpy -0.10 eV. This may be due to the large size of the i4 site, which is also the most favourable site for accommodation of transition metal interstitials. All other orientations exhibit moderate to large positive binding energies, and as such it is predicted that there is no driving force for the formation of interstitial clusters, except on the i4 site.

In addition to simple interstitial and vacancy clusters, antisite clusters are also possible.
Table 4.7: Binding energies of Be$_i$Be$_j$ with respect to two Be$_{i2}$. Negative values mean binding is favourable and positive unfavourable.

<table>
<thead>
<tr>
<th>Interstitial sites</th>
<th>Be$_{12}$V</th>
<th>Be$_{12}$Ti</th>
<th>Be$_{12}$Mo</th>
<th>Be$_{12}$W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be$<em>{i2}$Be$</em>{i2}$</td>
<td>0.38</td>
<td>0.71</td>
<td>0.37</td>
<td>0.42</td>
</tr>
<tr>
<td>Be$<em>{i3}$Be$</em>{i1}$ (in plane)</td>
<td>1.90</td>
<td>2.41</td>
<td>2.18</td>
<td>2.32</td>
</tr>
<tr>
<td>Be$<em>{i3}$Be$</em>{i1}$ (out plane)</td>
<td>1.98</td>
<td>2.50</td>
<td>2.10</td>
<td>2.22</td>
</tr>
<tr>
<td>Be$<em>{i3}$Be$</em>{i2}$</td>
<td>0.34</td>
<td>0.17</td>
<td>0.69</td>
<td>0.71</td>
</tr>
<tr>
<td>Be$<em>{i3}$Be$</em>{i3}$</td>
<td>1.69</td>
<td>2.50</td>
<td>1.82</td>
<td>1.86</td>
</tr>
<tr>
<td>Be$<em>{i3}$Be$</em>{i4}$ (in plane)</td>
<td>1.74</td>
<td>2.17</td>
<td>2.01</td>
<td>2.16</td>
</tr>
<tr>
<td>Be$<em>{i3}$Be$</em>{i4}$ (out plane)</td>
<td>1.96</td>
<td>2.42</td>
<td>0.69</td>
<td>0.71</td>
</tr>
<tr>
<td>Be$<em>{i4}$Be$</em>{i2}$</td>
<td>0.43</td>
<td>0.38</td>
<td>0.32</td>
<td>0.38</td>
</tr>
<tr>
<td>BeBe$_{i4}$</td>
<td>-0.10</td>
<td>-0.10</td>
<td>0.08</td>
<td>0.09</td>
</tr>
</tbody>
</table>

In particular, given the large size difference between the transition metal species and beryllium species, it was postulated that the accommodation of a transition metal atom on two beryllium sites (M$_{BeBe}$) may be favourable by comparison to accommodation on a single site. To test this, the binding energies of the reaction of V$_{Be}$ and M$_{Be}$ to form M$_{BeBe}$ are presented in table 4.8.

Several orientations of the M$_{BeBe}$ cluster exhibit strongly negative binding energy, with the lowest binding energy being for the M$_{Be2Be2}$ cluster in Be$_{12}$Ti and Be$_{12}$W (-3.02 and -4.55 eV respectively), and the M$_{Be2Be3}$ (out of plane) cluster for Be$_{12}$V and Be$_{12}$Mo (-2.46 and -2.88 eV respectively). It is interesting to note that the M$_{Be2Be2}$ cluster corresponds roughly to the arrangement of atoms in the P$_c$/mmm Be$_{17}$M$_2$ structure, which may explain why this defect is so favourable, although, it is not immediately apparent why there is such a large difference in binding energy of the M$_{Be2Be2}$ cluster between Be$_{12}$Ti/W and Be$_{12}$V/Mo.
Table 4.8: Binding enthalpy of $\text{M}_{\text{BeBe}}$ with respect to $\text{M}_{\text{Be2}}$ and $\text{V}_{\text{Be2}}$. Negative values mean binding is favourable and positive unfavourable.

<table>
<thead>
<tr>
<th>Anti-site vacancy pair</th>
<th>$\text{E}_B$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{M}_{\text{Be3Be3}}$ (in plane)</td>
<td>0.33 1.35 0.63 -1.77</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be3Be3}}$ (out of plane)</td>
<td>-0.42 0.17 -0.16 -1.28</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be2Be3}}$ (in plane)</td>
<td>-0.51 -0.09 -0.45 -1.48</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be2Be3}}$ (out of plane)</td>
<td>-2.46 -0.91 -2.88 -2.04</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be2Be2}}$ (in plane)</td>
<td>-0.40 4.26 -0.02 -1.77</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be2Be2}}$ (out of plane)</td>
<td>3.44 0.00 -0.32 -1.67</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be2Be1}}$</td>
<td>-0.06 -0.38 -0.16 -2.22</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be1Be3}}$</td>
<td>0.75 -0.46 0.54 -1.93</td>
</tr>
<tr>
<td>$\text{M}_{\text{Be1Be2}}$</td>
<td>0.75 0.00 0.03 -1.01</td>
</tr>
</tbody>
</table>

4.5 Nonstochiometry

When used as neutron multipliers, $^9$beryllium in these materials will be depleted through (n,2n) reactions, releasing radiogenic helium and tritium. This will alter the stoichiometry of the material over time. It is therefore important to understand the stability of the $\text{Be}_{12}M$ phases with decreasing beryllium content. This is achieved first through convex hull analysis [78] of all the Be-$M$ compounds that have been reported, to establish which are stable at 0 K, followed by examination of the deviation from stoichiometry of the $\text{Be}_{12}M$ phases. Examining the non-stoichiometry of the $\text{Be}_{12}M$ phase requires the defect analysis presented in sections 4.2-4.4 and knowledge of the nearest stable reference phase, as will be calculated through the complex hull analysis.

Complex hull analysis was performed by minimising all structures that have been reported in each Be - $M$ phase diagram (see figure 1.13 section 1.6), even those that are not reported to be stable at 0 K for completeness. This was repeated with the PBE and LDA exchange-correlation functionals since they typically overbind and underbind.
respectively, therefore providing an upper and lower bound on the stability of phases. The results of the convex hull analysis are shown in figure 4.2.

Phases corresponding to points that define the convex line of lowest energy (coloured points) are those that are predicted to be stable. Phases corresponding to points above this line are predicted to be unstable. While the results calculated with the LDA and PBE functionals are for the most part in qualitative agreement, the PBE functional predicts intermetallic phases to be significantly more stable relative to the elemental metal. This is consistent with the fact that LDA calculations are known to over-delocalise electrons, which may lead to an apparent increase in stability of the parent metals. In addition, the simulations with the PBE functional predict the Be$_{22}M$ phase to be stable for all systems, while simulations with the LDA simulation do not. Neither of these is consistent with experimental results, with the Be$_{22}M$ phase having been observed (at room temperature) for Be$_{22}$Mo and Be$_{22}$W, but not Be$_{22}$V and Be$_{22}$Ti. In the Be-Ti and Be-V systems the PBE functional predicts the Be$_{22}M$ phase to be only just below the line created between pure Be and the Be$_{12}M$ phase, thus suggesting it is only just stable. As such, it is possible that it is destabilised by temperature effects at elevated temperatures. Further, the phase transformation to form the Be$_{22}M$ phase would require long range diffusion, which would inhibit its formation at low temperature.

The convex hull diagram for the Be-Mo and Be-W systems calculated with the PBE functional (figure 4.2) are in complete agreement with the experimental phase diagrams (chapter 1, figure 1.13, with only three stable phases: Be$_2M$, Be$_{12}M$ and Be$_{22}M$. An additional BeMo$_3$ phase was identified by a single experimental study [203], however this was not corroborated by subsequent experiments, and is predicted to be unstable by these calculations.
Figure 4.2: Figure 3 - Convex hull analysis calculated using the LDA and PBE functionals of the Be-Ti, Be-V, Be-Mo and Be-W. Phases exhibiting positive formation energies (relative to end members) are not included.
The Be-Ti and Be-V phase diagrams include significantly more intermetallic phases. The simulated results using the PBE functional are in agreement with experiment regarding the stability of Be$_2$V, Be$_2$Ti, Be$_{17}$V$_2$, Be$_{17}$Ti$_2$, Be$_{12}$V and Be$_{12}$Ti, however Be$_{22}$Ti, Be$_{22}$V and Be$_3$V are also predicted to be stable, while Be$_3$Ti is predicted to be unstable by a small margin. Again, it should be noted that the formation energies of these phases lie extremely close to the boundary of stability. Thus, these discrepancies are likely attributed to temperature effects (both enthalpy and entropy), which may stabilise one phase relative to another. This has previously been shown to be the case for the closely-related Be-Fe and Be-Fe-Al systems [78].

Despite the discrepancies between the experimental and predicted stabilities of the Be-Ti and Be-V systems, it is still possible to investigate the deviation from stoichiometry of the Be$_{12}$M phases. This is achieved by considering the energy to dissolve a formula unit of the nearest 0 K reference state into the Be$_{12}$M phase (or vice versa) to form defects on the Be$_{12}$M lattice. An example of this is incorporation of Be$_{17}$Ti$_2$ into Be$_{12}$Ti to form beryllium vacancies:

$$\text{Be}_{17}\text{Ti}_2 + 7\text{Be} \rightarrow 7\text{V}_{\text{Be}} + 2\text{Be}_{12}\text{Ti} \quad (4.6)$$

where Be$_{\text{Be}}$ are Be atoms on Be sites in the host Be$_{12}$Ti lattice. A complete list of the equations used to calculate the formation energy of defects from the nearest reference state is presented in table 4.10. Reference states are chosen based on the convex hull analysis presented in figure 4.2. The minimum energy (since given the number of possible vacancy and interstitial sites in Be$_{12}$M there is a range of energies) for incorporation of the reference states is shown in table 4.9.

Using these results, the Arrhenius approximation is used to calculate the total defect
4.5. Nonstoichiometry

Table 4.9: Solution energy to closest compositional reference state that results in the formation of a single defect and hence a change in stoichiometry. Defect equations can be found in table 4.10.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Be$_{12}$Ti</th>
<th>Be$_{12}$V</th>
<th>Be$_{12}$Mo</th>
<th>Be$_{12}$W</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{Be}$</td>
<td>1.52</td>
<td>1.53</td>
<td>1.36</td>
<td>1.26</td>
</tr>
<tr>
<td>$V_{M}$</td>
<td>3.34</td>
<td>3.23</td>
<td>1.46</td>
<td>1.41</td>
</tr>
<tr>
<td>$Be_i$</td>
<td>2.49</td>
<td>2.34</td>
<td>2.23</td>
<td>2.37</td>
</tr>
<tr>
<td>$M_i$</td>
<td>6.04</td>
<td>5.39</td>
<td>5.64</td>
<td>6.76</td>
</tr>
<tr>
<td>$Be_M$</td>
<td>2.79</td>
<td>2.66</td>
<td>0.81</td>
<td>0.88</td>
</tr>
<tr>
<td>$M_{Be}$</td>
<td>2.98</td>
<td>1.78</td>
<td>2.39</td>
<td>4.67</td>
</tr>
<tr>
<td>$M_{2Be}$</td>
<td>1.48</td>
<td>0.84</td>
<td>0.88</td>
<td>1.38</td>
</tr>
<tr>
<td>$V_{Be}V_{Be}$</td>
<td>2.82</td>
<td>2.97</td>
<td>2.64</td>
<td>2.49</td>
</tr>
<tr>
<td>$V_{M}V_{Be}$</td>
<td>4.45</td>
<td>4.19</td>
<td>2.54</td>
<td>2.47</td>
</tr>
<tr>
<td>$V_{M}V_{M}$</td>
<td>7.18</td>
<td>7.17</td>
<td>3.50</td>
<td>3.54</td>
</tr>
<tr>
<td>$Be_iBe_i$</td>
<td>4.89</td>
<td>4.59</td>
<td>4.54</td>
<td>4.82</td>
</tr>
</tbody>
</table>

population for beryllium rich and deficient environments, $n_d$ at elevated temperatures:

$$n_d = N \exp\left(\frac{-E_f}{2k_B T}\right)$$  \hspace{1cm} (4.7)

Where $N$ is the number of available defect sites and $k_B$ is Boltzmann constant. From this, the maximum allowable deviation from stoichiometry before it is favourable to form a second phase has been calculated. This is presented in figure 4.3.
Table 4.10: Defect equations and associated reference states evaluated to calculate non-stochiometry.

<table>
<thead>
<tr>
<th>Material</th>
<th>Be\textsubscript{12}W and Be\textsubscript{12}Mo</th>
<th>Be\textsubscript{12}Ti and Be\textsubscript{12}V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference states</td>
<td>Be\textsubscript{22}W/Be\textsubscript{2}W, Be\textsubscript{22}Mo/Be\textsubscript{2}Mo</td>
<td>Be/Be\textsubscript{17}Ti\textsubscript{2}, Be/Be\textsubscript{17}V\textsubscript{2}</td>
</tr>
<tr>
<td>V\textsubscript{Be}</td>
<td>Be\textsubscript{2}M + 10Be\textsubscript{Be} ⇔ 10V\textsubscript{Be} + Be\textsubscript{12}M</td>
<td>Be\textsubscript{17}M\textsubscript{2} + 7Be\textsubscript{Be} ⇔ 7V\textsubscript{Be} + 2Be\textsubscript{12}M</td>
</tr>
<tr>
<td>V\textsubscript{M}</td>
<td>6Be\textsubscript{22}M + 5M\textsubscript{M} ⇔ 5V\textsubscript{M} + 11Be\textsubscript{12}M</td>
<td>12Be + M\textsubscript{M} ⇔ V\textsubscript{M} + Be\textsubscript{12}M</td>
</tr>
<tr>
<td>Be\textsubscript{i}</td>
<td>Be\textsubscript{22}M ⇔ 10Be\textsubscript{i} + Be\textsubscript{12}M</td>
<td>Be\textsubscript{17}M\textsubscript{2} + 8Be ⇔ 2Be\textsubscript{12}M + Be\textsubscript{i}</td>
</tr>
<tr>
<td>M\textsubscript{i}</td>
<td>6Be\textsubscript{2}M ⇔ 5M\textsubscript{i} + Be\textsubscript{12}M</td>
<td>12Be\textsubscript{17}M\textsubscript{2} ⇔ 7M\textsubscript{i} + 17Be\textsubscript{12}M</td>
</tr>
<tr>
<td>2V\textsubscript{Be}</td>
<td>Be\textsubscript{2}M + 10Be\textsubscript{Be} ⇔ 5(2V\textsubscript{Be}) + Be\textsubscript{12}M</td>
<td>2Be\textsubscript{17}M\textsubscript{2} + 14Be\textsubscript{Be} ⇔ 7(2V\textsubscript{Be}) + 4Be\textsubscript{12}M</td>
</tr>
<tr>
<td>2V\textsubscript{M}</td>
<td>12Be\textsubscript{22}M + 5M\textsubscript{M} ⇔ 5(2V\textsubscript{M}) + 22Be\textsubscript{12}M</td>
<td>24Be + 2M\textsubscript{M} ⇔ (2V\textsubscript{M}) + 2Be\textsubscript{12}M</td>
</tr>
<tr>
<td>V\textsubscript{Be}V\textsubscript{M}</td>
<td>11Be\textsubscript{22}M + 10M\textsubscript{M} + 10Be\textsubscript{Be} ⇔ 10V\textsubscript{Be}V\textsubscript{M} + 21Be\textsubscript{12}M</td>
<td>11Be + Be\textsubscript{Be} + M\textsubscript{M} ⇔ V\textsubscript{Be}V\textsubscript{M} + Be\textsubscript{12}M</td>
</tr>
<tr>
<td>2Be\textsubscript{i}</td>
<td>Be\textsubscript{22}M ⇔ 5(2Be\textsubscript{i}) + Be\textsubscript{12}M</td>
<td>2Be\textsubscript{17}M\textsubscript{2} + 16Be ⇔ 4Be\textsubscript{12}M + 2Be\textsubscript{i}</td>
</tr>
<tr>
<td>Be\textsubscript{M}</td>
<td>13Be\textsubscript{22}M + 10M\textsubscript{M} ⇔ 10Be\textsubscript{M} + 23Be\textsubscript{12}M</td>
<td>13Be + Be\textsubscript{Be} + M\textsubscript{M} ⇔ Be\textsubscript{M} + Be\textsubscript{12}M</td>
</tr>
<tr>
<td>M\textsubscript{Be}</td>
<td>13Be\textsubscript{2}M + 10Be\textsubscript{Be} ⇔ 10M\textsubscript{Be} + 3Be\textsubscript{12}M</td>
<td>2Be\textsubscript{17}M\textsubscript{2} + Be\textsubscript{Be} + Be ⇔ M\textsubscript{Be} + 3Be\textsubscript{12}M</td>
</tr>
<tr>
<td>M\textsubscript{2Be}</td>
<td>14Be\textsubscript{2}M + 20Be\textsubscript{Be} ⇔ 10M\textsubscript{2Be} + 4Be\textsubscript{12}M</td>
<td>2Be\textsubscript{17}M\textsubscript{2} + 2Be\textsubscript{Be} ⇔ M\textsubscript{2Be} + 3Be\textsubscript{12}M</td>
</tr>
</tbody>
</table>
Figure 4.3: Phase field lines predicted from total defect concentrations calculated using the Arrhenius approximation for materials with an excess of beryllium and transition metal.

All compounds exhibit very little deviation from stochiometry in particular for Be$_{12}$Ti (note the very small x axis limits in figure 4.3 of 0.1% M). Be$_{12}$V may accommodate some limited beryllium sub-stoichiometry, Be$_{12}$Mo may accommodate small deviation on both sides of the stoichiometric composition and Be$_{12}$W very minor levels of beryl-
4.5. Nonstochiometry

Beryllium hyper-stoichiometry, but only at elevated temperatures. These differences are due to the relative energy of the three lowest energy defect reactions which form \( V_{\text{Be}} \), \( M_{\text{Be}} \) and \( M_{\text{BeBe}} \). In \( \text{Be}_{12}\text{Ti} \), the defect with the lowest energy is \( \text{Ti}_{\text{BeBe}} \) with energy of 1.48 eV. This is considerably higher than for other materials, and limits deviation from stoichiometry. For \( \text{Be}_{12}\text{V} \), \( V_{\text{BeBe}} \) also has the lowest formation energy (0.84 eV), which is significantly lower than in \( \text{Be}_{12}\text{Ti} \) and thus allows inclusion of excess transition metal. This is similar for \( \text{Be}_{12}\text{Mo} \), where the \( \text{Mo}_{\text{BeBe}} \) species has a formation energy of 0.88 eV, although \( \text{Be}_{\text{Mo}} \) has a formation energy 0.81 eV, which allows for some non-stoichiometry in the beryllium rich region. The lowest energy defect in \( \text{Be}_{12}\text{W} \) is \( \text{W}_{\text{Be}} \) with an energy of 0.88 eV, thus allowing for hyperstoichiometry.

Given the very small magnitude of nonstoichiometry predicted in these materials, even at elevated temperature, they may effectively be considered line compounds. The implication for their use as neutron multipliers is that to account for beryllium depletion through \((n,2n)\) reactions, it may be useful to manufacture them with excess beryllium as a second phase. This is beneficial from a manufacturing perspective as it increases the very limited ductility of the compounds. If excess beryllium is not included, these materials are likely to form secondary phases with compositions \( \text{Be}_{17}\text{V}_2 \), \( \text{Be}_{17}\text{Ti}_2 \), \( \text{Be}_2\text{W} \) and \( \text{Be}_2\text{Mo} \) as beryllium depletion proceeds. \( \text{Be}_{12}\text{Ti} \) and \( \text{Be}_{12}\text{V} \) are likely to be the least effected by the formation of these secondary phases, not because they can accommodate excess non-stoichiometry, but because the \( \text{Be}_{17}M_2 \) phase bears clear structural relation to the \( \text{Be}_{12}M \) phase (as explored in chapter 3) and has similar composition. As such, it is suggested that \( \text{Be}_{22}\text{Mo} \) and \( \text{Be}_{22}\text{W} \) might be considered as neutron multipliers over \( \text{Be}_{12}\text{Mo} \) and \( \text{Be}_{12}\text{W} \). This is further supported by their superior neutronic properties, as preliminary studies have shown that a sufficient tritium breeding ratio cannot be achieved with current module designs and the use of \( \text{Be}_{12}\text{W} \) [56].
4.6 Defect Migration in Be$_{12}$Ti

In addition to the enthalpy of formation of defects and clusters, how defects move and interact will also determine the rate at which they coalesce to form larger extended defects such as dislocations and voids. To date, migration of intrinsic defects has not been investigated in any of these materials. To address this, the work presented in this section explores intrinsic defect migration in Be$_{12}$Ti, the most attractive candidate for use as a neutron multiplier. The Linear Synchronous Transit (LST), Quadratic Synchronous Transit (QST) and Nudged Elastic Band (NEB) methods [141, 142] were used within the DFT framework (as outlined in chapter 2). These methods are significantly more computationally expensive than simple geometry optimisations, limiting the number of simulations that could be performed. As such, it was decided to focus on only one material (i.e. Be$_{12}$Ti) so that a more comprehensive investigation could be undertaken.

Diffusion in any material is limited by both the concentration of defects (which, for equilibrium defect populations is determined by their formation energy) and the energy for the defect to move from one site to another (the hopping energy, $E_{\text{hop}}$). Based on the investigations of defect formation energies, intrinsic defect populations will likely be dominated by Schottky disorder and beryllium Frenkel disorder, resulting in high populations of V$_{\text{Be}}$, V$_{\text{Ti}}$ and Be$_{\text{i}}$ relative to other defects. Given the negative binding enthalpy to form V$_{\text{Be}}$V$_{\text{Be}}$ and the strongly negative binding enthalpy to form V$_{\text{Be}}$V$_{\text{Ti}}$, it is likely these will also contribute to the defect population. As such, in addition to point defects, migration of these species is considered.
4.6. Defect Migration in $\text{Be}_{12}\text{Ti}$

4.6.1 Point Defect Migration

Vacancy migration was investigated between all symmetrically distinct nearest neighbour combinations. This was achieved by first geometry optimising the vacant sites, to a low energy tolerance of $10^{-9}$ eV/atom, a force tolerance of $10^{-4}$ (eV/Å) per atom, and stress tolerance of $10^{-3}$ (eV/Å) per atom. Such tight tolerances are necessary to ensure the correct transition path is found, as the NEB method may be confused if another minima (however shallow) exists between the reactant and the product. Given the computational expense of the NEB method, rather than applying it to all possible migration pathways, the LST and QST methods were used to identify the energy of the transition state in order to select candidates to be investigated with the full NEB methodology. These energies are shown for vacancy migration in table 4.11 where, for example $V_{\text{Be}1} \rightarrow V_{\text{Be}3}$ is shorthand for:

$$V_{\text{Be}1} + \text{Be}_{\text{Be}3} \rightarrow \text{Be}_{\text{Be}1} + V_{\text{Be}3}$$

Table 4.11: Calculated hopping energies for beryllium and titanium vacancies in $\text{Be}_{12}\text{Ti}$. The reactant (R) is the initial state and product (P) the final state.

<table>
<thead>
<tr>
<th>Sites for vacancy hops</th>
<th>$E_{\text{hop}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From R</td>
</tr>
<tr>
<td>$V_{\text{Be}1} \rightarrow V_{\text{Be}1}$</td>
<td>0.76</td>
</tr>
<tr>
<td>$V_{\text{Be}1} \rightarrow V_{\text{Be}3}$</td>
<td>6.98</td>
</tr>
<tr>
<td>$V_{\text{Be}2} \rightarrow V_{\text{Be}1}$</td>
<td>0.91</td>
</tr>
<tr>
<td>$V_{\text{Be}2} \rightarrow V_{\text{Be}2}$ in plane</td>
<td>0.50</td>
</tr>
<tr>
<td>$V_{\text{Be}2} \rightarrow V_{\text{Be}2}$ out of plane</td>
<td>5.14</td>
</tr>
<tr>
<td>$V_{\text{Be}2} \rightarrow V_{\text{Be}2}$ in plane</td>
<td>4.07</td>
</tr>
<tr>
<td>$V_{\text{Be}2} \rightarrow V_{\text{Be}3}$ in plane</td>
<td>6.40</td>
</tr>
<tr>
<td>$V_{\text{Be}2} \rightarrow V_{\text{Be}3}$</td>
<td>7.85</td>
</tr>
<tr>
<td>$V_{\text{Be}3} \rightarrow V_{\text{Be}3}$ out of plane</td>
<td>3.07</td>
</tr>
<tr>
<td>$V_{\text{Be}3} \rightarrow V_{\text{Be}3}$ in plane</td>
<td>1.05</td>
</tr>
<tr>
<td>$V_{\text{Ti}} \rightarrow V_{\text{Ti}}$</td>
<td>6.75</td>
</tr>
</tbody>
</table>
Several beryllium vacancy hops have an energy around or below one eV when the vacancy is exchanged between the following sites $\text{Be}_1 \rightarrow \text{Be}_1$ (0.76 eV), $\text{Be}_2 \rightarrow \text{Be}_1$ (0.91 eV), $\text{Be}_2 \rightarrow \text{Be}_2$ in plane (0.50 eV) and $\text{Be}_3 \rightarrow \text{Be}_3$ in plane (1.05 eV). The only direct $V_{\text{Ti}}$ migration route (in the [001] direction) has a transition state energy of 6.75 eV, significantly higher than for $V_{\text{Be}}$ mediated mechanisms. The transition states with energy lower than 1.0 eV are visualised in figure 4.4, along with the transition for $V_{\text{Ti}}$. NEB calculations were performed using the transition state identified by the LSTQST simulations for the same pathways. Energy profiles of hopping pathways calculated using NEB are also shown in figure 4.4.

From figure 4.4, it is clear that the lowest energy vacancy hop, between two $\text{Be}_2$ sites does not itself permit long range diffusion, as there are no further neighbouring in-plane $\text{Be}_2$ sites for further hops (i.e. there is no contiguous pathway). This is also the case for the $V_{\text{Be}_3} \rightarrow V_{\text{Be}_3}$ transition which has energy 1.05 eV. Of course, these transitions may be components in contiguous pathways. The lowest energy pathway that allows long range diffusion (i.e. the lowest energy contiguous pathway) is from $\text{Be}_1 \rightarrow \text{Be}_1$, with an energy of 0.76 eV, although this is limited to the [001] direction. Diffusion in other directions is facilitated by a the $\text{Be}_1 \rightarrow \text{Be}_2$ vacancy hop with energy 0.91 eV, which connects to the $V_{\text{Be}_2} \rightarrow V_{\text{Be}_2}$ pathway (i.e. $V_{\text{Be}_1} \rightarrow V_{\text{Be}_2} \rightarrow V_{\text{Be}_2} \rightarrow V_{\text{Be}_1}$, where the rate determining step is $V_{\text{Be}_2} \rightarrow V_{\text{Be}_2}$ with energy 0.91 eV). As such, it is predicted that Be vacancy diffusion is slightly anisotropic, favouring the [001] direction (0.76 eV compared to 0.91 eV).

Beryllium interstitial migration was investigated using the same approach. The transition state energy for beryllium migration between nearest neighbour symmetrically distinct interstitial sites was calculated using the LSTQST method, with energies reported in table 4.12. The pathways and energy profiles (as calculated using the NEB methodology) of the three lowest energy hops are shown in figure 4.5.
4.6. Defect Migration in $\text{Be}_{12}\text{Ti}$

Figure 4.4: Left: lowest energy migration pathways for beryllium and titanium vacancy migration in $\text{Be}_{12}\text{Ti}$. Right: NEB pathways for the lowest energy migration pathways.
Table 4.12: Calculated hopping energies for beryllium and titanium interstitials in Be$_{12}$Ti. The reactant (R) is the initial state and product (P) the final state.

<table>
<thead>
<tr>
<th>Sites</th>
<th>$E_{\text{hop}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>From R</td>
</tr>
<tr>
<td>Be$<em>{i2}$ → Be$</em>{i2}$</td>
<td>1.19</td>
</tr>
<tr>
<td>Be$<em>{i3}$ → Be$</em>{i1}$</td>
<td>5.10</td>
</tr>
<tr>
<td>Be$<em>{i3}$ → Be$</em>{i1}$</td>
<td>0.77</td>
</tr>
<tr>
<td>Be$<em>{i3}$ → Be$</em>{i2}$</td>
<td>0.42</td>
</tr>
<tr>
<td>Be$<em>{i1}$ → Be$</em>{i2}$</td>
<td>1.44</td>
</tr>
<tr>
<td>Ti$<em>{i2}$ → Ti$</em>{i4}$</td>
<td>1.00</td>
</tr>
<tr>
<td>Ti$<em>{i3}$ → Ti$</em>{i1}$</td>
<td>7.20</td>
</tr>
<tr>
<td>Ti$<em>{i2}$ → Ti$</em>{i3}$</td>
<td>6.92</td>
</tr>
</tbody>
</table>

The lowest energy contiguous pathway is via the $i_2$ sites with hopping energy 1.20 eV (which also have the lowest interstitial formation energy of 1.86 eV). This pathway proceeds only in the [001] direction. The next lowest energy paths, which are also both contiguous, are from $i_3$ to $i_1$ and $i_3$ to $i_2$ with hopping energies of 1.29 eV and 2.42 eV respectively. It should be noted that both the $i_1$ and $i_3$ sites have significantly higher formation energy (3.19 eV and 3.69 eV respectively), and thus migration through these sites is further energetically challenged. As such, it is predicted that beryllium interstitial migration in Be$_{12}$Ti will be strongly anisotropic favouring the [001] direction via the $i_2$ sites.

For titanium interstitials, the lowest energy contiguous pathway is via the $i_2$ and $i_4$ sites, with hopping energy 1.00 eV. This pathway only allows diffusion in the [001] direction. The next lowest energy pathways are from the $i_3$ to $i_1$ site and the $i_2$ to $i_3$ sites, with hopping energy 7.20 and 6.92 eV respectively. Other potential pathways investigated were all found to be energetically extremely unfavourable (with hopping energy in excess of 15 eV), and thus are not reported here. Based on these results, it is expected that Ti$_i$ migration will be strongly anisotropic.
4.6. Defect Migration in $\text{Be}_{12}\text{Ti}$

![Diagram of defect migration pathways in $\text{Be}_{12}\text{Ti}$](image)

Figure 4.5: Left: lowest energy migration pathways for Be and Ti interstitial migration in $\text{Be}_{12}\text{Ti}$. Beryllium lattice sites have been omitted for legibility. Right: NEB pathways for the lowest energy migration pathways.

### 4.6.2 Cluster Migration

As several vacancy clusters were shown to have negative binding enthalpy, they are likely to be significant to the defect chemistry, therefore it is necessary to investigate migration via such processes. In particular, some $\text{V}_{\text{Be}}\text{V}_{\text{Be}}$ and $\text{V}_{\text{Be}}\text{V}_{\text{Ti}}$ clusters were shown to be especially favourable, thus the migration of these species has been investigated. This proved somewhat difficult due to the large number of starting configurations: to investigate transitions between all 9 identified $\text{V}_{\text{Be}}\text{V}_{\text{Be}}$ configurations would require 72 simulations. This is significantly reduced by accounting for symmetry of the lattice to 21 possible transitions.

Transitions are assumed to proceed by exchange of a single vacancy (e.g. the shorthand $\text{V}_{\text{Be}3}\text{V}_{\text{Be}2} \rightarrow \text{V}_{\text{Be}2}\text{V}_{\text{Be}2}$ where a beryllium atom moves from the Be2 site to the Be3 site). Given the large number of transitions, the NEB methodology proved too
4.6. Defect Migration in Be$_{12}$Ti

computationally expensive, thus only LSTQST results are presented. The results of LSTQST calculations for all identified V$_{Be}$V$_{Be}$ and V$_{Be}$V$_{Ti}$ divacancy transitions are shown in table 4.13.

Table 4.13: Hopping energy barrier to exchange one vacancy within beryllium and beryllium-titanium divacancies in Be$_{12}$Ti.

<table>
<thead>
<tr>
<th>transition</th>
<th>$E_{\text{hop}}$ (eV) from R</th>
<th>$E_{\text{hop}}$ (eV) from P</th>
<th>transition</th>
<th>$E_{\text{hop}}$ (eV) from R</th>
<th>$E_{\text{hop}}$ (eV) from P</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be2}$ (1)</td>
<td>4.01</td>
<td>3.72</td>
<td>V$<em>{Be2}$V$</em>{Be3}$ → V$<em>{Be1}$V$</em>{Be3}$</td>
<td>3.53</td>
<td>3.82</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be2}$ (2)</td>
<td>1.17</td>
<td>0.77</td>
<td>V$<em>{Be3}$V$</em>{Be3}$ → V$<em>{Be1}$V$</em>{Be3}$</td>
<td>0.71</td>
<td>0.77</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be3}$ (1)</td>
<td>0.63</td>
<td>0.53</td>
<td>V$<em>{Be3}$V$</em>{Be3}$ → V$<em>{Be2}$V$</em>{Be1}$</td>
<td>0.74</td>
<td>0.53</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be2}$ (2)</td>
<td>1.08</td>
<td>0.86</td>
<td>V$<em>{Be2}$V$</em>{Be3}$ → V$<em>{Be2}$V$</em>{Be3}$</td>
<td>1.35</td>
<td>1.24</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be1}$ (3)</td>
<td>1.08</td>
<td>0.76</td>
<td>V$<em>{Be2}$V$</em>{Be3}$ → V$<em>{Be1}$V$</em>{Be3}$</td>
<td>0.98</td>
<td>0.64</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be3}$ (2)</td>
<td>7.41</td>
<td>5.59</td>
<td>V$<em>{Be2}$V$</em>{Be3}$ → V$<em>{Be2}$V$</em>{Be1}$</td>
<td>0.48</td>
<td>0.37</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be3}$ (3)</td>
<td>4.58</td>
<td>4.65</td>
<td>V$<em>{Be2}$V$</em>{Be3}$ → V$<em>{Be1}$V$</em>{Be3}$ (2)</td>
<td>1.20</td>
<td>0.98</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be1}$ (2)</td>
<td>0.73</td>
<td>0.70</td>
<td>V$<em>{Be2}$V$</em>{Ti}$ → V$<em>{Be1}$V$</em>{Ti}$</td>
<td>0.95</td>
<td>0.53</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be3}$ (4)</td>
<td>0.94</td>
<td>1.27</td>
<td>V$<em>{Be2}$V$</em>{Ti}$ → V$<em>{Be2}$V$</em>{Ti}$</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be3}$ (5)</td>
<td>0.97</td>
<td>1.15</td>
<td>V$<em>{Be3}$V$</em>{Ti}$ → V$<em>{Be1}$V$</em>{Ti}$</td>
<td>0.68</td>
<td>0.71</td>
</tr>
<tr>
<td>V$<em>{Be2}$V$</em>{Be2}$ → V$<em>{Be2}$V$</em>{Be1}$ (3)</td>
<td>0.76</td>
<td>0.69</td>
<td>V$<em>{Be1}$V$</em>{Ti}$ → V$<em>{Be1}$V$</em>{Ti}$</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>V$<em>{Be1}$V$</em>{Be1}$ → V$<em>{Be2}$V$</em>{Be1}$</td>
<td>0.62</td>
<td>0.99</td>
<td>V$<em>{Be3}$V$</em>{Ti}$ → V$<em>{Be2}$V$</em>{Ti}$</td>
<td>0.83</td>
<td>0.45</td>
</tr>
<tr>
<td>V$<em>{Be1}$V$</em>{Be1}$ → V$<em>{Be2}$V$</em>{Be3}$</td>
<td>0.70</td>
<td>0.95</td>
<td>V$<em>{Be3}$V$</em>{Ti}$ → V$<em>{Be3}$V$</em>{Ti}$</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>V$<em>{Be3}$V$</em>{Be3}$ → V$<em>{Be2}$V$</em>{Be3}$</td>
<td>0.90</td>
<td>1.30</td>
<td>V$<em>{Be1}$V$</em>{Ti(000)}$ → V$<em>{Be1}$V$</em>{Ti(1\frac{1}{2} \frac{1}{2} \frac{1}{2})}$</td>
<td>6.03</td>
<td>6.03</td>
</tr>
<tr>
<td>V$<em>{Be3}$V$</em>{Ti(000)}$ → V$<em>{Be3}$V$</em>{Ti(001)}$</td>
<td>4.44</td>
<td>4.44</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The lowest energy contiguous migration pathway associated with a beryllium divacancy is a combination of the V$_{Be2}$V$_{Be3}$ → V$_{Be2}$V$_{Be1}$ → V$_{Be2}$V$_{Be2}$ → V$_{Be2}$V$_{Be3}$ hops (i.e. a Be atom moves to a vacant Be3 site, then a Be2 atom moves to a vacant i1 site, and finally a Be3 atom moves to a vacant Be2 site), with rate determining energy 0.76 eV. This forms a full isotropic diffusion pathway. As such, diffusion of V$_{Be}$V$_{Be}$ can be considered isotropic with hopping energy of 0.76 eV. This is approximately the same energy as for a single Be vacancy.

Migration of V$_{Be}$V$_{Ti}$ can be conceptualised as a two step process due to the large discrepancy of migration energy between V$_{Be}$ and V$_{Ti}$: 1) rotation of the V$_{Be}$ species around V$_{Ti}$ followed by 2) hopping of V$_{Ti}$. The latter of these processes has the higher
energy and is thus the rate limiting step. Two migration pathways have been identified, one of which is anisotropic and another which is isotropic.

Diffusion of $V_{Be}V_{Ti}$ in the [001] direction may occur via the $V_{Be3}V_{Ti(000)} \rightarrow V_{Be3}V_{Ti(001)}$ reaction, which has energy of 4.44 eV. Following this, for diffusion to proceed further the $V_{Be}$ species must orientate around the $V_{Ti}$ site, the lowest energy pathway being $V_{Ti}V_{Be3} \rightarrow V_{Ti}V_{Be2} \rightarrow V_{Ti}V_{Be3}$ with energy 0.83 eV. Isotropic diffusion may proceed via the $V_{Be1}V_{Ti(000)} \rightarrow V_{Be1}V_{Ti(\frac{1}{2}\frac{1}{2}1)}$ reaction, which has energy 6.03 eV. For diffusion to proceed in the [001] direction, the $V_{Be1}$ species must orientate around $V_{Ti(\frac{1}{2}\frac{1}{2}\frac{1}{2})}$ from $V_{Be1(\frac{1}{2}\frac{1}{2}\frac{1}{2})}$ to $V_{Be1(\frac{1}{2}\frac{1}{2}\frac{1}{2})}$ with energy 0.80 eV. For diffusion to proceed isotropically, the $V_{Be1}$ species must then orientate around $V_{Ti(\frac{1}{2}\frac{1}{2}1)}$ from $V_{Be1(\frac{1}{2}\frac{1}{2}\frac{1}{2})}$ to $V_{Be1(\frac{1}{2}\frac{1}{2}\frac{1}{2})}$, the lowest energy pathway for which is $V_{Ti}V_{Be1} \rightarrow V_{Ti}V_{Be3} \rightarrow V_{Ti}V_{Be1}$ and has energy 0.71 eV. Given that titanium migration via the Be3 site is lower in energy than via the Be1 site, and lower than that for $V_{Ti}$ migration (6.75 eV) it is predicted that titanium vacancy diffusion will be anisotropic in $Be_{12}Ti$ favouring the [001] direction. The energy of this pathway is however significantly higher than for a titanium interstitial in the [001] direction (1.05 eV), which is expected to be the dominant diffusion mechanism for titanium in this material. While this energy is comparable to that for migration of a beryllium vacancy, given the significantly higher formation energy of a titanium interstitial, beryllium diffusion overall has a significantly lower activation energy.

4.7 Summary and Conclusions

The intrinsic defect properties of $Be_{12}Ti$, $Be_{12}V$, $Be_{12}Mo$ and $Be_{12}W$ have been predicted using DFT simulations. Formation energies for common point defects, including vacancies, interstitials and antisite defects. Further, four stable intrinsic interstitial sites have been identified in the $I_4/mmm$ structure for the first time.
4.7. Summary and Conclusions

Defects on the beryllium sublattice have consistently lower formation enthalpy than on the transition metal sublattice. For beryllium vacancies, the Be2 lattice site has the lowest formation enthalpy for all materials studied (1.20-1.48 eV), although all three Be sites are relatively close in energy (0.2 eV). Transition metal vacancies have formation energy between 3.16 eV and 4.10 eV, with Be_{12}W having the lowest and Be_{12}Ti the highest. These results are in excellent qualitative agreement with previous studies of Be_{12}W [96]. For beryllium interstitials, only three sites are stable. These are the i1, i2 and i3 sites, of which the i2 site has the lowest formation energy for all materials, from 1.86 eV in Be_{12}Ti to 2.50 eV in Be_{12}W. The other sites have formation energy between 0.92 eV and 1.83 eV higher than the i2 site. Transition metal interstitials can be accommodated in all three sites, as well as an additional i4 (4c) site. The i4 site has the lowest formation energy for transition metal interstitials, ranging from 4.19 eV in Be_{12}Ti to 5.96 eV in Be_{12}W. Antisites, consisting of beryllium accommodated on a transition metal site have formation energies between 3.55 eV for Be_{12}Ti and 2.76 eV for Be_{12}W, while for a transition metal accommodated on a beryllium site, the Be2 site has the lowest formation enthalpy, from 0.95 eV in Be_{12}Ti to 3.81 eV in Be_{12}W.

During radiation damage, defects are formed through intrinsic disorder processes, typically Frenkel, Schottky and Antisite disorder. Using the calculated defect energies, it is predicted that Schottky disorder has the lowest energy (1.35 - 1.66 eV/defect), although beryllium Frenkel disorder has similar energy in Be_{12}V and Be_{12}Ti.

Small clusters including beryllium divacancies and interstitials, mixed divacancies and the accommodation of a transition metal on two beryllium sites were investigated. Some beryllium and mixed divacancies exhibit negative binding energy (i.e. their formation is favourable), although this is strongly orientation dependent. Only one beryllium di-interstitial orientation exhibits modest negative binding energy in Be_{12}Ti, while all other combinations for all materials exhibit positive binding energy.
Several orientations of beryllium divacancy accommodate a transition metal with negative binding energy, with $M_{\text{Be}_2\text{Be}_2}$ exhibiting strongly negative binding energy in $\text{Be}_{12}\text{Ti}$ and $\text{Be}_{12}\text{W}$ (-3.02 eV and -4.55 eV respectively) and $M_{\text{Be}_2\text{Be}_3}$ exhibiting strongly negative binding energy in $\text{Be}_{12}\text{V}$ and $\text{Be}_{12}\text{Mo}$ (-2.46 eV and -2.88 eV respectively). This is attributed to the large size discrepancy between beryllium and the transition metal, which leads to large strains when the transition metal is accommodated on an interstitial site or as a simple antisite defect.

Convex hull analysis of the Be-V/Ti/Mo/W systems was undertaken using both the PBE and LDA functionals. It was found that the PBE functional is more consistent with observed results, correctly predicting the stability of all structures in the Be-Mo and Be-W systems. In the Be-Ti and Be-V systems, simulations with the PBE functional predict the $\text{Be}_{22}M$ phase to be stable, while this phase has not been observed experimentally. $\text{Be}_3\text{V}$ is also predicted to be stable contrary to experimental observations. As these phases lie close to the bounds of stability, it is hypothesised that they may only be stable at low temperatures, which could inhibit their formation on kinetic grounds.

Nonstoichiometry was predicted in the $\text{Be}_{12}M$ materials using the calculated defect energies and convex hull analysis. All materials exhibit only very limited nonstoichiometry, in particular $\text{Be}_{12}\text{Ti}$. $\text{Be}_{12}\text{V}$ exhibits limited hyperstoichiometry, and $\text{Be}_{12}\text{Mo}$ limited hypo and hyperstoichiometry. This suggests it is advisable to manufacture these materials with an excess of beryllium for neutron multiplying applications, since will be depleted by the transmutation process.

Point defect and cluster migration for $\text{Be}_{12}\text{Ti}$ was investigated using the LST, QST and NEB methodologies. Defect species were investigated based on their predicted concentrations from analysis of defect energies. Migration of beryllium vacancies is predicted to have hopping energy of 0.76 eV in the [001] direction via Be1 sites, and
hopping energy of 0.91 eV for isotropic diffusion via Be1 and Be2 sites. As such, vacancy diffusion is predicted to be weakly anisotropic. Ti vacancy migration is predicted to only occur in the [001] direction with energy 6.75 eV.

Beryllium interstitial migration is predicted to exhibit a hopping energy of 1.19 eV in the [001] direction and occurs via Be2 sites. Isotropic diffusion may be mediated by the i2, i3 and i1 sites, with hopping energy of 2.42 eV. Titanium interstitial migration may occur restricted to the [001] direction via the i2 and i4 sites with hopping energy of 1.00 eV. This is significantly lower than for any isotropic diffusion pathway (hopping energy > 6.92 eV). As such both beryllium and titanium interstitial migration is predicted to strongly favour the [001] direction.

Beryllium divacancy migration is predicted to be isotropic, with hopping energy of 0.66 eV via the $V_{\text{Be2Be2}}$, $V_{\text{Be2VB3}}$ and $V_{\text{Be2Be1}}$ species, although there are several other transitions with only slightly higher energy. Mixed beryllium-titanium divacancy diffusion is limited by migration of the titanium vacancy, which has a hopping energy of 6.03 eV for isotropic diffusion, and 4.44 eV for migration in the [001] direction.

Given intrinsic defect populations at thermal equilibrium are predicted to be dominated by beryllium vacancies, divacancies, and, to a lesser extent, beryllium interstitials, it is predicted that overall beryllium migration will be weakly anisotropic favouring the [001] direction. Further, titanium migration has significantly higher migration energy than beryllium.
Chapter 5

Displacement Processes in Fusion Materials

This work is published in:

5.1 Introduction

As discussed in section 1.7, the threshold displacement energy, $E_d$, is an important materials property that can be used to quantify radiation damage in a material. It is an important parameter for models such as those due to Kinchin-Pease (KP) [105], Norgett-Robinson-Torrens (NRT) [106] and Greenwood [107], which are used to estimate the number of point defects created during a displacement cascade. By extension, if the flux profile of the incident radiation is known, then the total number of point defects created in the material can be estimated. This is key to predict the forma-
5.1. Introduction

ion of extended defects that are responsible for many of the deleterious effects on the macroscopic properties of materials. Further, \( E_d \) is an important parameter in the popular SRIM software \([110]\), which uses a binary collision model to calculate the final distribution of atomic displacements in a material, caused by incident energetic ions.

Despite being so important to the modelling of radiation damage, \( E_d \) has no consistent definition, which complicates attempts to calculate it. This stems, in part, from the fact that the probability of displacement (\( P_d \)) is not a step function with primary knock on energy, \( E \). Instead, \( P_d \) increases as a curve, approaching a value of one almost asymptotically \([205]\). This is primarily due to two physical effects. Firstly, at finite temperature, atoms in the material are vibrating while confined to their potential well with some kinetic energy, which has an additive effect to the energy resulting from the primary collision. More significantly, \( E_d \) is also strongly dependent on crystallographic orientation. It is possible to define a probability of displacement for each lattice direction, \( P_d(\theta, \phi) \), and further a threshold displacement energy, \( E_d(\theta, \phi) \). To generate the average probability of displacement, \( \bar{P}_d \) (as would be measured experimentally for a polycrystalline sample), \( P_d(\theta, \phi) \) must be averaged across all directions:

\[
\bar{P}_d = \frac{\int_0^{2\pi} \int_0^\pi P_d(\theta, \phi)\sin\theta d\theta d\phi}{\int_0^{2\pi} \int_0^\pi \sin\theta d\theta d\phi}
\] (5.1)

From the perspective of MD simulations, this can either be achieved by a random sampling of directions (providing the sample size is large enough) \([206]\) or through uniform spatial sampling \([205]\).

Because \( \bar{P}_d \) is not a step function, the cutoff for \( E_d \) has been variously defined as occurring either at the lowest energy with non-zero probability of displacement, \( \bar{E}_{d,0} \), displacement probability of 0.1, \( \bar{E}_{d,0.1} \) or displacement probability of 0.5 \( \bar{E}_{d,0.5} \) \([207]\).
5.1. Introduction

Further, it is not immediately clear which of these measures would be more appropriate for use with models such as KP.

Experimentally, $E_d$ is measured by varying the energy of an electron beam incident upon the material, and measuring changes in the resistivity, which would indicate the formation of defects. As such, it is likely that this is measuring $E_{d,0}$, thus this measure will be used in this work so that results may be more easily compared with experimental data.

In addition to directional effects, the definition of $E_d$ has been further complicated since the advent of atomistic simulation as a tool to model it. Using atomistic simulation, the displacement event can be directly simulated and monitored, allowing for the detection of atomic displacements that do not form defects (i.e. whereby two atoms of the same species switch lattice sites during the displacement event). Thus, $E_d$ must be further differentiated into $E_{d,\text{disp}}$, which is the threshold energy for displacement, regardless of whether a defect is formed, and $E_{d,\text{def}}$, the threshold energy to create a defect. The latter of these is more easily directly compared to experimental values, and is thus more useful for quantifying radiation damage, given it is the point defects produced that are ultimately responsible for the changes in materials properties. $E_{d,\text{disp}}$ is, however, useful as a point of comparison for $E_{d,\text{def}}$, as the difference between the two may be useful for examining the role of recovery immediately following the displacement event.

In this chapter the displacement behaviour of beryllium, tungsten, carbon, and tungsten carbide is investigated using molecular dynamic simulations. These materials were chosen due to the availability and suitability of interatomic potentials, their relevance as materials for fusion, and in order to investigate the effect of local environment on $E_d$. In SRIM, the approximation made is that $E_d$ is a unique function of the PKA species,
and no account is taken of the local environment. Previous MD studies comparing the displacement behaviour of Ti and O in TiO$_2$ have shown marked difference between different crystal structures, challenging this approximation [208]. An aim of this work is to investigate this further by comparing displacement behaviour between different allotropes of carbon, and between elemental carbon and tungsten, and tungsten carbide.

5.2 Threshold Displacement in Beryllium

Despite being used in nuclear applications for over 70 years, there has been little investigation of low energy displacement processes in beryllium, although there has been significant investigation, both experimental and simulated, of radiation damage in general [15, 64]. As such, in this section displacement processes in beryllium are explored. This is achieved using two interatomic potentials, as described in chapter 2.

5.2.1 Computational Details

Preliminary investigations began using the EAM potential developed and parameterised by Agrawal et al [149] (henceforth refered to as the Agrawal potential). This potential was selected as it provides a good approximation of several materials properties of beryllium, including lattice parameters, elastic constants, melting temperature and defect energies (see table 2.2). A key consideration for displacement simulations, that is not normally fit to for more general empirical potentials, is the repulsive force at short interatomic separations. For the Agrawal potential, the repulsive force due to the overlap of electronic orbitals is modelled by a strongly repulsive embedding function for high electron densities. Often, repulsive forces are modelled by a splined
5.2. *Threshold Displacement in Beryllium*

ZBL potential \[110, 207\], which is well characterised and has been shown to provide a good approximation of such forces at low interatomic separations. However, given that the repulsive force is encoded in the multi-body terms of the Agrawal potential, it proved impossible to retroactively spline a ZBL potential to the pair potential. Consequently, a second potential was employed: a bond order potential parameterised by Björkas et al \[153\](henceforth referred to as the Björkas potential). This potential has the benefit that, as well as reproducing many physical properties with similar accuracy to the Agrawal potential, it has had a ZBL potential splined using the methodology of Nordlund et al. \[207\], giving confidence that it accurately reproduces the repulsive term at short interatomic separations.

Displacement simulations were performed in $15 \times 15 \times 10$ supercells of beryllium containing 4500 atoms. Cells were first geometry optimised and equilibrated to 300 K for a minimum of 50 ps with a timestep of 0.2 fs in the NPT ensemble, during which temperature and pressure were controlled using the Berendsen thermostat and barostat \[209\]. To calculate the probability of displacement for each energy and direction, each simulation must be repeated with different starting configurations. For this work, simulations were repeated 20 times with starting configurations generated by equilibrating the supercells for additional increments of 1 ps.

Simulations proceeded by imparting a central atom in the equilibrated supercell with energies between 4-100 eV in increments of 4 eV for the Björkas potential, and 12-200 eV for the Agrawal potential. From the initial impact, supercells were run in the NVE ensemble for 20,000 timesteps of 0.01 fs, 10,000 timesteps of 0.1 fs and 10,000 timesteps of 1.0 fs for a total simulation time of 12.6 ps. Such a short timestep is necessary in the collisional phase due to the very high velocity of the PKA.
The crystallographic directions investigated were based on a segment of a geodesic projection of directions representing at least twice the irreducible symmetry of the crystal. For HCP beryllium this is an arc from $0-120^\circ \theta$ and $0-90^\circ \phi$, with a spacing of $6^\circ$ in both $\theta$ and $\phi$.

In the first study, the distinction between defect formation ($P_{\text{def}}^d$) and displacement ($P_{\text{disp}}^d$) was not made, and thus simulations using the Agrawal potential only examined displacement. In the second study, using the Björkas potential, both defect formation and displacement were investigated. An atom was considered displaced if during the simulation, it was ‘permanently’ displaced (i.e. until the end of the simulation) by half of the equilibrium bond length (or more). Defects were identified using local environment analysis, as implemented by P. Fossati [210]. In this method, the tridimensional local average density field is used to characterise the local environment of atoms and generate a configuration graph. Vacancies and interstitials create unique patterns in this configuration graph thereby facilitating identification. Contrary to other commonly used defect detection methods, this approach requires no reference state, is readily adaptable to different crystal structures, and can reliably differentiate between different types of defects such as vacancies, interstitials and split interstitials.

### 5.2.2 Directionally Averaged Results and Analysis

The directionally averaged probability of displacement, $\bar{P}_{\text{disp}}^d$, and probability of defect formation, $\bar{P}_{\text{def}}^d$, are presented with increasing primary knock on energy, $E$, in figure 5.1. Directionally averaged threshold displacement ($\bar{E}_{\text{disp}}^d$) and threshold defect formation energy $\bar{E}_{\text{def}}^d$ are calculated from this data using the Robinson model [205], which relates...
5.2. Threshold Displacement in Beryllium

Figure 5.1: Values of $\bar{P}_d^{\text{disp}}$ simulated using the Björkas and Agrawal potentials, and values of $\bar{P}_d^{\text{def}}$ for the Björkas potential. Lines are the Robinson model fitted to the simulated data.

$P_d$ and $\bar{E}_d$ at low $E$:

$$\bar{P}_d(E) = \begin{cases} 
0 & E \leq \bar{E}_d \\
\frac{1}{\beta} [E^\alpha - \bar{E}_d^\alpha] & E \geq \bar{E}_d 
\end{cases}$$  \hspace{1cm} (5.2)

In this scheme, $\beta$ and $\alpha$ are fitting constants. To calculate $E_d$ from this model, a least squares fitting scheme was used to fit the model to the simulated $\bar{P}_d$ curve below a displacement probability of 0.75. From this model, $\bar{E}_d^{\text{disp}}$ and $\bar{E}_d^{\text{def}}$ were calculated to be $8.67 \pm 0.29$ and $9.15 \pm 0.92$ eV for the Björkas potential, and $\bar{E}_d^{\text{disp}}$ 34.80$\pm$0.55 eV for the Agrawal potential. Examining the correspondence between the Robinson model and simulated $\bar{P}_d$ curves in fig 5.1, the model reproduces the simulated data at low $E$, and around the onset of non zero $P_d$, giving confidence in the calculated value of $\bar{E}_d$. The model does, however, overpredict $\bar{P}_d^{\text{disp}}$ at higher $E$, where $\bar{P}_d^{\text{disp}}$ approaches one, as there is no inherent mechanism in the model to prevent it surpassing unity, which is clearly unphysical. As such, this model is not suitable to predict displacement probability at higher energy.
Examining the correspondence between the $\bar{P}^{\text{disp}}$ and $\bar{P}^{\text{def}}$ curve for the Björkas potential, at low $E$ they are in close agreement, and consequently predict similar values of $\bar{E}_d$, however at higher energies $\bar{P}^{\text{disp}}$ is significantly higher than $\bar{P}^{\text{def}}$. This suggests that at these energies, significant recombination of defects occurs immediately following the displacement event.

$\bar{E}^{\text{disp}}$ predicted by the Björkas potential (8.67 eV) is significantly lower than that predicted by the Agrawal potential (34.80 eV). The reason for this large difference may be due to the gradient of each potential energy surface at short interatomic distances, which has previously been shown to have a large effect on $\bar{E}_d$ [207]. In order to investigate this, presented in figure 5.2 is the energy ($E$) for a beryllium atom in bulk beryllium, displaced from its lattice site towards a nearest neighbour by displacement, $x$, for both the Agrawal and Björkas potentials. The Björkas potential has a gradient approximately quarter that of the Agrawal potential. This may be an important contributing factor to the difference in $\bar{E}^{\text{disp}}$.

$\bar{E}^{\text{def}}$ predicted by the Björkas potential (9.15 eV) is significantly below that used in the SRIM model (25 eV) [110], but is consistent with the work of Borodin et al. [211] who predicted a value around 10 eV using classical MD, and around 20 eV using quantum-MD (although it should be noted that value suffers from a lack of statics and small supercell size, which is known to artificially increase $\bar{E}^{\text{def}}$ [207]).

In addition to $\bar{E}^{\text{def}}$ and $\bar{E}^{\text{disp}}$, it is useful to examine the maximum displacement, $x_m$, from which $\bar{E}^{\text{disp}}$ is calculated. $\bar{x}_m$ as a function of $E$ is presented in figure 5.3. For both potentials, at low $E$, $\bar{x}_m$ remains approximately constant around 0.43 Å. This is of similar magnitude to that which may be expected due to thermal oscillations of the atoms around their lattice sites. Beyond 35 and 10 eV for the Agrawal and Björkas potentials respectively, the displacement increases gradually to a maximum of around...
Figure 5.2: Potential energy (E) for an atom displaced toward its nearest neighbour by displacement (x) in bulk beryllium at 0 K, as evaluated using the Agrawal and Björkas potentials [153, 149].

4 Å and 8 Å at 200 eV and 100 eV respectively. The cut-off at which $\bar{x}_m$ begins to increase is similar to $E_{\text{disp}}$ as calculated using the Robinson model, which would be expected given the close relation of $\bar{x}_m$ and $P_{\text{disp}}$. Based on these observations, maximum displacement as a function of E may be described in a similar manner to the Robinson model.

Exactly what form a model should take above $E_{\text{disp}}$ is not immediately apparent. A first approach is to treat the material as a continuum force field that exerts a drag force on the PKA. This can be modelled in two ways: either with the drag force ($F_D$) proportional to the momentum of the PKA or as proportional to the kinetic energy of the PKA. This gives the following two equations:

$$F_D = \alpha m \frac{dx}{dt}$$  
\hspace{1cm} (5.3)

$$F_D = \frac{\beta m}{2} \left( \frac{dx}{dt} \right)^2$$  
\hspace{1cm} (5.4)
where $\alpha$ is the drag coefficient in the momentum model, $\beta$ the drag coefficient in the kinetic energy dependent model and $m$ the mass of the PKA. The acceleration can be calculated from the force from Newton’s second law of motion to give:

$$m \frac{d^2x}{dt^2} - \alpha m \frac{dx}{dt} = 0 \quad (5.5)$$

$$m \frac{d^2x}{dt^2} - m \frac{\beta}{2} \left( \frac{dx}{dt} \right)^2 \quad (5.6)$$

These equations can be solved to yield the displacement, $x$, given the boundary conditions that at $t=0$, $\frac{dx}{dt} = \sqrt{\frac{2E}{m}}$ and $x = 0$:

$$x = \frac{1}{\alpha} \sqrt{\frac{2E}{m}} \left(e^{\frac{\alpha t}{m}} - 1\right) \quad (5.7)$$

$$x = \frac{2}{\beta} \ln\left(\frac{c}{c + \frac{\beta t}{2}}\right), \quad c = -\frac{2E_d}{m}^{-1/2} \quad (5.8)$$

Figure 5.3: Simulated maximum displacement with increasing $E$ for the Agrawal potential (left) and Björkas potential (right). Lines denote the fitted momentum based model (m1) and kinetic energy based model (m2).
To calculate $\bar{x}_m$ as a function of $E$, at the limit where $E = \bar{E}_d$ the equations become:

$$x = \frac{1}{\alpha} \sqrt{\frac{2E}{m} \left( \sqrt{\frac{\bar{E}_d}{E}} - 1 \right)} \quad (5.9)$$

$$x = \frac{2}{\beta} \ln \left( \frac{\bar{E}_d}{E} \right) \quad (5.10)$$

These equations are valid when $E > \bar{E}_d$, below which they have no physical significance. Below $\bar{E}_d$, it is expected that some atomic displacement, $x_0$, will originate from the motion of atoms localised about their site. Thus, to completely describe the low $E$ regime, equations 5.9 and 5.10 become:

$$\bar{x}_m = x_0$$

$$x_m = \frac{1}{\alpha} \sqrt{\frac{2E}{m} \left( \sqrt{\frac{\bar{E}_d}{E}} - 1 \right)} + x_0 \quad \left\{ \begin{array}{l} E < \bar{E}_d \\ \bar{E}_d > E \end{array} \right. \quad (5.11)$$

$$\bar{x}_m = x_0$$

$$x_m = \frac{2}{\beta} \ln \left( \frac{\bar{E}_d}{E} \right) + x_0 \quad \left\{ \begin{array}{l} E < \bar{E}_d \\ \bar{E}_d > E \end{array} \right. \quad (5.12)$$

These models are fitted to the simulated results in figure 5.3 for the Agrawal and Björkas potentials. Both models reproduce the simulated results with reasonable accuracy, however for the Björkas potential the kinetic energy model overestimates $\bar{x}_m$ at moderate $E$ and underestimates it at high $E$. It is unclear which of these models is more suitable, however there is prescience for an energy dependent correction in the NRT model which predicts the number of displaced atoms and which includes an energy dependent efficiency.

5.2.3 Directional Results

Having examined the directionally averaged results, it is now important to examine the directional dependence of threshold displacement in beryllium. Figure 5.4 presents
schematic projections in the [0001] direction of $E_{\text{disp}}^d(\theta, \phi)$ and $E_{\text{disp}}^{d,50}(\theta, \phi)$ for both potentials, as well as $E_{\text{def}}^d(\theta, \phi)$ and $E_{\text{def}}^{d,50}(\theta, \phi)$ for the Björkas potential. On first inspection, there are strong qualitative similarities for both potentials across all measures of $E_d$. The directions with lowest $E_d$ correspond to nearest neighbour directions: $\langle 11\bar{2}0 \rangle$ in the basal plane and $\langle 2\bar{1}\bar{1}\bar{1} \rangle$ out of plane. This is consistent with the work of Thomas et al. [212], who investigated $E_d(\theta, \phi)$ in rutile using similar methodology. It was found that displacement events in nearest neighbour directions caused a collision sequence resulting in a larger separation of the interstitial-vacancy pair, which were thus more likely to remain stable. Directions corresponding to glancing angle collisions have the highest $E_d$ across all measures and both potentials. Such collisions would effectively divide the kinetic energy between the PKA and the impacted atom, thus dissipating the energy in a small volume of material, not only making displacement less likely but also promoting recombination.

Beyond the qualitative similarities, there are significant quantitative differences between the two sets of results. For the Agrawal potential, $E_{\text{disp}}^d$ varies from 35 eV to 60 eV, while for the Björkas potential it varies from 8 to 20 eV. This is similar for $E_{\text{disp}}^{d,50}$, which varies from 40 to 95 eV and 8 to 28 eV for the Agrawal and Björkas potential respectively. Again, this may be explained by the relative “hardness” of the Agrawal potential by comparison to the Björkas potential. Comparing $E_{\text{disp}}^d$ and $E_{\text{def}}^d$ for the Björkas et al. potential, there is little quantitative difference, however this is not the case for $E_{\text{disp}}^{d,50}$ and $E_{\text{def}}^{d,50}$, with the latter covering a higher range of energies (12-55 eV by comparison to 8-28 eV). This reflects the trends seen in the directionally averaged results, and confirms that recombination is significant at high $E$, at least using the Björkas potential.
5.3 Carbon, Tungsten and Tungsten Carbide

To further explore the dependence of displacement behaviour on local environment as well as atomic species, low energy displacement simulations were performed in diamond, graphite, tungsten and tungsten carbide. These materials were selected for several reasons. Firstly, tungsten is currently used as a divertor material in fusion reactors, and tungsten carbide is under consideration for the same application, thus it is important to understand displacement processes in these materials. Further, graphite is one of the most widely used and consequently best characterised nuclear materials, thus there is an abundance of experimental data available for comparison. Finally, a consistent, well characterised interatomic potential set, with specific consideration of short range

Figure 5.4: Stereographic projections of $E_d(\theta, \phi)$ in Be in the [0001] direction. $E_{d,0}$ (the lowest energy with non-zero probability of displacement) is shown top and $E_{d,0}$ (the lowest energy with displacement probability of 0.5) is shown bottom.

5.3 Carbon, Tungsten and Tungsten Carbide

...
interactions, has been developed for the tungsten-carbon system by Juslin et al. [146] for modelling nuclear fusion materials. This potential set is further part of an even wider self-consistent potential set for all fusion materials: beryllium-tungsten-carbon-hydrogen-helium (which includes the Björkas potential) leaving open the option of extending this work to other fusion relevant materials.

5.3.1 Computational Details

Following from the experience of modelling threshold displacement in beryllium, the same general methodology was used (i.e. supercells were set up and equilibrated in the same way, and displacement simulations proceeded in the same manner). Like for beryllium, supercells with approximately 5000 atoms and uniform dimensions were created. For diamond this corresponds to an $8 \times 8 \times 8$ supercell containing 4096 atoms, BCC tungsten a $15 \times 15 \times 15$ supercell containing 6750 atoms, and hexagonal tungsten carbide a $14 \times 14 \times 14$ supercell containing 5488 atoms. As mentioned in chapter 2, one limitation of the Juslin potential is that it does not adequately describe Van-der-Waals interactions, which are significant in graphite; they are the primary interactions between individual layers of graphene [164]. As a result, the way in which graphene sheets slip over each other is not modelled well. As such, a larger graphite $24 \times 24 \times 7$ supercell containing 16128 atoms was used to limit slip as far as possible. Despite this, some interlayer slip continued to occur, with the unintended consequence that no distinction can be made between the two graphene sites in this model, as these sites differ only in their position relative to carbon atoms in neighbouring graphene sheets.

To produce a representative sample of lattice directions, a geodesic projection of directions with spacing of $6^\circ$ was investigated. For all materials, at least double the irreducible symmetry of the structure was simulated. For graphite and tungsten car-
bide, this is from 0-120° θ and 0-90° φ, tungsten 0-90° θ and φ, and diamond 0-180° θ and 0-90° φ.

Defects and displacements were detected in the same way as described for beryllium in section 5.2.1. It should be noted, however, that because the magnitude of vibrations within single graphene sheets in the graphite structure are often greater than the nearest neighbour bond length, displacement detection based on maximum distance travelled is impossible in this structure. Further, given the large strain within graphene sheets that these vibrations cause, the local tridimensional averaging method of defect detection also proved unreliable. Instead, a simple coordination based approach, in which the local coordination environment is compared to the perfect cell, was used to detect defects. Comparison to manual inspection of defect cells showed perfect correspondence, thus this method can be considered to be reliable.

5.3.2 Directionally Averaged Results

Simulated results for $\bar{P}_d^{\text{disp}}$ and $\bar{P}_d^{\text{def}}$ as a function of E with the fitted Robinson model are shown in figures 5.5.a and 5.5.b respectively. $\bar{E}_d^{\text{disp}}$ and $\bar{E}_d^{\text{def}}$ as calculated using the fitted Robinson model are presented in table 5.1.

Observation of figure 5.5.a shows that the Robinson model closely reproduces the simulated $\bar{P}_d^{\text{def}}$ as a function of E. There are significant differences between the $\bar{P}_d^{\text{def}}$ curves for carbon in diamond, graphite and tungsten carbide, as well as for tungsten in BCC tungsten and tungsten carbide. This leads to significantly different values of $\bar{E}_d^{\text{def}}$ for carbon in graphite (3.58 eV), diamond (19.8 eV) and tungsten carbide (22.2 eV), as well as for tungsten in BCC tungsten (38.0 eV) and tungsten carbide (45.0 eV). This is contrary to the common approximation that $\bar{E}_d^{\text{def}}$ is solely species dependent, and instead suggests that it is also strongly dependent on the local environment of the displaced
Figure 5.5: $\bar{P}_{\text{def}}^d$ and $\bar{P}_{\text{disp}}^d$ calculated from displacement simulations for diamond, graphite, tungsten, and tungsten and carbon PKAs in tungsten carbide. Lines are those from the Robinson model fitted to the simulated data, which is used to predict $\bar{E}_d$ as presented in table 5.1.

species. Previous MD studies by Robinson et al. [208] have also shown this to be the case for TiO$_2$, with the simulated $\bar{E}_d$ varying significantly between different phases for both oxygen and titanium PKAs.

That $\bar{E}_{\text{def}}^d$ is lower in pure tungsten than in tungsten carbide may in part be correlated with the higher bulk modulus (443 GPa) and tungsten Frenkel pair formation energy (15.7 eV) of tungsten carbide in comparison to tungsten (308 GPa and 10.01 eV) [146].

For carbon, $\bar{E}_{\text{def}}^d$ is significantly lower for graphite than diamond, and $\bar{P}_{\text{def}}^d$ is significantly higher across all energies, approaching unity at around 50 eV. $\bar{E}_{\text{def}}^d$ for carbon is even higher in tungsten carbide than diamond, although at energies above 96 eV there is a higher probability of a defect being formed in tungsten carbide. This is counter to the Kinchin-Pease model, which predicts $\bar{P}_{\text{def}}^d$ solely based on $\bar{E}_{\text{def}}^d$ (below the threshold for electronic stopping), but can be consistent with the NRT and Greenwood models which include a damage efficiency factor. A similar picture emerges for tungsten
Table 5.1: Threshold displacement values calculated using the Robinson model. \( \bar{E}_{\text{disp}} \) is not available for graphite due to large vibrations in the graphene sheets, which makes displacement an unreliable measure in this material. Error is the standard error.

<table>
<thead>
<tr>
<th>Material and PKA</th>
<th>( \bar{E}_{\text{def}} ) (eV)</th>
<th>( \bar{E}_{\text{disp}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>19.8±0.3</td>
<td>12.9±0.7</td>
</tr>
<tr>
<td>Graphite</td>
<td>3.58±0.7</td>
<td>-</td>
</tr>
<tr>
<td>BCC Tungsten</td>
<td>38.0±0.8</td>
<td>36.7±0.7</td>
</tr>
<tr>
<td>Tungsten carbide (W PKA)</td>
<td>45.0±1.1</td>
<td>27.0±1.8</td>
</tr>
<tr>
<td>Tungsten carbide (C PKA)</td>
<td>22.2±0.7</td>
<td>22.0±0.9</td>
</tr>
</tbody>
</table>

in BCC tungsten and tungsten carbide, since although BCC tungsten has lower \( \bar{E}_{\text{def}} \), above 62 eV there is a higher probability of forming a defect in tungsten carbide.

To aid in understanding the differences between species in different environments, it is useful to examine the \( \bar{P}_{\text{disp}} \) curves in figure 5.5.b. As mentioned previously, data is not available for graphite due to the large magnitude of vibrations in single graphene sheets, which mask displacement from impact events. Examining the \( \bar{P}_{\text{disp}} \) curve for diamond, \( \bar{P}_{\text{disp}} \) is significantly higher than \( \bar{P}_{\text{def}} \) across all energies above \( \bar{E}_{\text{disp}} \). Further, \( \bar{P}_{\text{disp}} \) reaches near unity around 40 eV. The diamond \( \bar{P}_{\text{disp}} \) curve bears qualitative similarity to the graphite \( \bar{P}_{\text{def}} \), albeit with slightly higher \( \bar{E}_{\text{d}} \) (3.6 and 12.9 eV respectively). This suggests that one of the reasons for the large discrepancy between the \( \bar{P}_{\text{def}} \) curves for diamond and graphite, is that defect recovery is much more probable in diamond. It does not, however, explain the lower value of \( \bar{E}_{\text{def}} \) in graphite. The \( \bar{P}_{\text{disp}} \) curve for carbon in tungsten carbide is similar to the \( \bar{P}_{\text{def}} \) curve, although the probability of displacement is only slightly higher across all energies than the probability of defect formation. This suggests that defect recombination during the displacement event is not a significant effect in this material.
5.3. Carbon, Tungsten and Tungsten Carbide

The $P_{\text{disp}}$ curve for a tungsten PKA in BCC tungsten is similar to the $P_{\text{disp}}$ curve at low energies, however at higher energies $P_{\text{disp}}$ is significantly higher than $P_{\text{def}}$ suggesting that defect recombination occurs immediately following the collisional phase. The curve for a tungsten PKA in tungsten carbide is similar to that in BCC tungsten, although it has slightly lower $E_{\text{disp}}$.

The simulated $P_{\text{disp}}$ for both carbon and tungsten PKAs in tungsten carbide deviates significantly from the Robinson model. In particular, at energies around $E_{\text{disp}}$ predicted by the Robinson model, $P_{\text{disp}}$ is significantly greater than that predicted by the Robinson model. As $x_m$ is calculated for all species, this may be explained by the possibility of energy transfer and thus displacement of species other than the PKA. To explore this possibility, the $P_{\text{def}}$ curves for both carbon and tungsten PKAs are separated by defect species in figure 5.6.

![Figure 5.6](image)

Figure 5.6: $P_{\text{def}}$ curves for W and C PKAs in tungsten carbide, showing total defect formation probability, and probability of defect formation on the carbon and tungsten sublattices. Dashed lines show one standard deviation. Drop charts show the fraction of tungsten (blue) and carbon (green) defects formed by each PKA.
For a tungsten PKA, at low energies defect formation occurs exclusively on the carbon sublattice, while at higher energies defects are formed on both sublattices. This is unsurprising given the significantly lower $\bar{E}_{d}^{\text{def}}$ of carbon in tungsten carbide, and further given the lower mass of carbon, should a tungsten PKA collide with carbon in a head on collision, almost all its kinetic energy would be transferred. Conversely, a carbon PKA only rarely causes tungsten displacements, as would be expected given their relative mass and $\bar{E}_{d}^{\text{def}}$. As such, while this effect explains the deviation of the simulated $\bar{P}_{d}^{\text{disp}}$ data from the Robinson model for a tungsten PKA, the cause of the deviation for a carbon PKA remains unexplained.

In order to examine the correspondence of simulated results with previous studies, simulated and experimental values of $E_{d}$ are presented in table 5.2. The simulated value for pure tungsten (38.0 eV) is similar to the experimental value (42.0 eV [213]), and lower than for previous MD studies [214, 215]. The simulated value for diamond (19.8 eV) is significantly lower than experimental values (35-47.6 eV [216, 217]), as is the simulated value for graphite (3.58 eV by comparison to 30-35.3 eV [218]). Given that simulated results are significantly lower for both carbon allotropes, this might be consistent with the potential used being “softer” than the real energy surface. Examining final configurations for the graphite structure provides another potential reason for the low $\bar{E}_{d}^{\text{def}}$ value. All defects below 20 eV occur as an “intimate vacancy-interstitial pair” (in the notation of [219]), whereby the PKA is displaced between the graphene sheets forming tetrahedral coordination with the sheet above. Such defects have been observed to form in previous threshold displacement simulations, and to have a formation energy of 15.7 eV [219]. The major difference between these simulations and the simulations performed herein, is that an additional force was applied between graphene sheets. As such, it is possible that the lack of force between graphene sheets in these simulations significantly reduces the formation energy of an intimate vacancy-interstitial
Table 5.2: Calculated threshold displacement values, experimental values ($\bar{E}_{\text{disp}}^{\text{exp}}$) and previous molecular dynamic results ($\bar{E}_{\text{disp}}^{\text{MD}}$) where available. $\bar{E}_{\text{disp}}^{\text{disp}}$ is not available for graphite due to large vibrations in the graphene sheets which make displacement an unreliable measure in this material. Error is the standard error.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\bar{E}_{\text{def}}$ (eV)</th>
<th>$\bar{E}_{\text{disp}}$ (eV)</th>
<th>$\bar{E}_{\text{disp}}^{\text{exp}}$ (eV)</th>
<th>$\bar{E}_{\text{disp}}^{\text{MD}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>19.8±0.3</td>
<td>12.9±0.7</td>
<td>37.5-47.6$^a$, 35$^b$</td>
<td>50$^c$</td>
</tr>
<tr>
<td>Graphite</td>
<td>3.58±0.7</td>
<td>-</td>
<td>33$^d$, 30-35.3$^e$</td>
<td>21$^f$, 20$^g$, 26$^h$</td>
</tr>
<tr>
<td>BCC Tungsten</td>
<td>38.0±0.8</td>
<td>36.7±0.7</td>
<td>42$^i$</td>
<td>41$^k$, 52-68$^l$</td>
</tr>
<tr>
<td>Tungsten carbide (W PKA)</td>
<td>45.0±1.1</td>
<td>27.0±1.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tungsten carbide (C PKA)</td>
<td>22.2±0.7</td>
<td>22.0±0.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>


pair, leading to an unphysically low $\bar{E}_{\text{def}}^{\text{disp}}$.

### 5.3.3 Directional Results

The directional dependence of $E_{\text{d}}$ in tungsten, graphite and diamond is presented in figure 5.7. This shows that $E_{\text{d}}^{\text{def}}$ in tungsten is strongly directionally dependent, although contrary to the trends observed in beryllium, nearest neighbour $\langle 111 \rangle$ directions have moderate $E_{\text{d}}^{\text{def}}$ (50 eV), while the $\langle 001 \rangle$ directions have the lowest $E_{\text{d}}^{\text{def}}$ (35 eV) and glancing angle collisions the highest (135 eV). A similar trend emerges for $E_{\text{d},50}^{\text{def}}$, although at higher energy.

That the $\langle 001 \rangle$ directions in tungsten have low $E_{\text{d}}^{\text{def}}$ may result from it being the direction to the octahedral interstitial site in the BCC structure, allowing for the direct formation of a Frenkel pair. Further, in contrast to HCP beryllium the BCC structure is not close packed, and thus the maximum angular distance to a neighbour for the $\langle 001 \rangle$ directions in the BCC structure is significantly greater than for any direction in the HCP structure (i.e. there is a larger gap).
Figure 5.7: Stereographic projections of $E_{\text{def}}^d(\theta, \phi)$ in the [0001] direction for tungsten, graphite and diamond ($E_{\text{disp}}^d(\theta, \phi)$ and $E_{\text{def}}^d(\theta, \phi)$).
5.3. *Carbon, Tungsten and Tungsten Carbide*

Examine the directional dependence of $E_{\text{d}}^{\text{def}}$ for graphite, results out of the (0001) plane should be treated with caution, given the preclusion for graphene sheets to slide over each other. It can be seen, however, that nearest (10\bar{1}0) neighbour directions have the highest $E_{\text{d}}^{\text{def}}$ (18 eV), followed by other directions in the (0001) plane (16 eV), whereas directions out of the (0001) plane have lower $E_{\text{d}}^{\text{def}}$ (3 eV), a trend replicated by the $E_{\text{d}}^{\text{def,50}}$ results. On examination of the final atomic configurations, it was found that displacements out of plane result in the formation of “intimate vacancy-interstitial pairs”, where the displaced atom is effectively pushed into tetrahedral coordination with an atom in the neighbouring graphene sheets. Previous studies have calculated the energy of such defects to be 15 eV [219], which is clearly inconsistent with the minimum 3 eV $E_{\text{d}}^{\text{def}}$ observed here. The difference is likely to be as a result of the inadequate description of interlayer forces, with the previous study adding an explicit interlayer force term to compensate. The lack of such a force significantly decreases the formation energy of the interstitial-vacancy pair, resulting in the abnormally low threshold displacement energy.

For diamond, $E_{\text{d}}^{\text{disp}}$ follows a similar trend to that observed for $E_{\text{d}}^{\text{def}}$ in tungsten, with $E_{\text{d}}^{\text{disp}}$ moderate in (111) nearest neighbour directions (28 eV), lowest in directions far from nearest neighbour (16 eV) and highest at glancing angles (36 eV), with the effect even more pronounced for $E_{\text{d}}^{\text{disp,50}}$. Comparing with $E_{\text{d}}^{\text{def}}$, there is no clear distinction between nearest neighbour and glancing angle collisions, although directions far from nearest neighbours still have lowest $E_{\text{d}}^{\text{def}}$. This is consistent with the hypothesis that glancing angle collisions promote defect recovery. $E_{\text{d}}^{\text{def,50}}$ follows similar trends to $E_{\text{d}}^{\text{def}}$, albeit with much higher energy (30-160 eV) and with significantly more scatter in the data. That this is significantly higher than $E_{\text{d}}^{\text{disp}}$ confirms that in these simulations significant defect recombination occurs at higher energies.
For both graphite and diamond the lowest $E_{\text{disp}}$ are in directions far from nearest neighbours. This may be a consequence of the strong directional bonding in these materials, which prevents recombination of “intimate vacancy-interstitial pairs”, whereas in metals such as beryllium and tungsten collisions in nearest neighbour directions are favoured for stable defect formation as the resultant defects have greater separation.

Having examined $E_{\text{def}}^d(\theta,\phi)$ for elemental materials, figure 5.8 presents $E_{\text{def}}^d(\theta,\phi)$ for tungsten and carbon PKAs in tungsten carbide. For the tungsten PKA, the lowest $E_{\text{def}}^d$ directions are the $\langle 2\overline{1}11 \rangle$ carbon nearest neighbour directions (35 eV), followed by the $\langle \overline{2}111 \rangle$ direction (45 eV), with directions surrounding the [0001] direction having highest $E_{\text{def}}^d$ (140 eV). For $E_{\text{def}}^d$, a similar trend emerges, although there is a clear prevalence for glancing angle interactions to have high $E_{\text{def}}^d$.

For carbon PKAs, the highest $E_{\text{def}}^d$ directions are those surrounding the $\langle 0001 \rangle$ direction (30 eV), while in other directions $E_{\text{def}}^d$ appears relatively constant around 20 eV, although this may simply be a result of insufficient energy resolution in the original simulations. Puzzlingly, $E_{\text{def}}^d_{d,50}$ shows a very different trend, so that directions with high $E_{\text{def}}^d$ around the [0001] direction having low $E_{\text{def}}^d_{d,50}$, which is similar to $E_{\text{def}}^d$ in those directions. Further, a clear prevalence for non-nearest neighbour directions in the (0001) plane emerges. It is unclear as to why these trends develop, however it may be a result of the strong directional bonding in this material and its more complex crystal structure.
5.4 Summary and Conclusions

Low energy displacement processes were simulated in beryllium using two different interatomic potential models. It was found that the directionally averaged probability of displacement increased above a cutoff energy in a fashion consistent with the Robinson model, which allowed the prediction of the threshold displacement energy with a high degree of confidence. It was found that the threshold displacement energy was 34.80 eV and 8.67 eV for the Agrawal and Björkas potential respectively, with the large difference being attributed to the Björkas potential being “softer” (i.e. having less steep energy gradients) at low interatomic separations (figure 5.2).
Although not investigated for the Agrawal potential, for the Björkas potential, at higher energies there is a significant difference between the probability of displacement and the probability to form a defect, suggesting significant defect recombination immediately following the displacement event. The threshold energy for defect formation predicted using the Björkas potential is 9.15 eV, which is consistent with other work that has used this potential but significantly lower than the 20 eV value predicted by ab-initio simulations (although the methodology of the study in question is predisposed to calculate higher threshold energies). Further, it is lower than the value commonly used in the SRIM code (25 eV) which has implications for its predictions when applied to beryllium.

The directional dependence of threshold displacement in beryllium with respect to the crystallographic lattice was also investigated. For both potentials, it was found that the $\langle 10\bar{1}0 \rangle$ and $\langle 2\bar{1}11 \rangle$ families of nearest neighbour directions have the lowest threshold displacement and (for the Björkas potential) threshold defect formation energies, while directions representing glancing angle collisions to these directions have the highest values. This was also true for the threshold at which there is a 50% chance of a defect forming, although there is significantly more scatter in that data. These results are consistent with the work of Bodorin et al. [21].

Displacement processes were also investigated in other fusion materials, namely carbon (both diamond and graphite), tungsten and tungsten carbide, in order to interrogate the common assumption that threshold displacement energy is solely species dependent. It was found that carbon has significantly different threshold defect formation energy in graphite (3.58 eV) in comparison to diamond (19.8 eV) and tungsten carbide (22.5 eV), as does tungsten in BCC tungsten (38.0 eV) and tungsten carbide (45.0 eV).
The reason for such a significant difference between carbon in graphite and diamond, and further the anonymously low value for graphite in comparison to experimental results, may be a result of inadequacies in the potential model. In particular, the model used does not account for interlayer forces between graphene sheets, which significantly reduces the formation energy of “intimate vacancy-interstitial pairs”, where the interstitial sits is in tetrahedral coordination between graphene planes. Further, significant defect combination is hypothesised to occur in the post ballistic phase in diamond, given the significant difference between the probability of displacement and of defect formation for this material at higher energies.

Directional dependence of threshold displacement and defect formation was investigated in these materials. For BCC tungsten, it was found that unlike beryllium, nearest neighbour \(\langle 111 \rangle\) directions have moderate threshold displacement energy, although directions indicating glancing angle collisions also have high threshold displacement energy. The lowest threshold displacement (and defect formation energies) are the \(\langle 001 \rangle\) directions, which correspond to the direction towards the octahedral interstitial site and is the furthest from nearest neighbour directions. Diamond showed a similar trend, with nearest neighbour directions having moderate threshold displacement and defect formation energies, while glancing angle directions have the highest. Graphite, due to the low formation barrier to intimate vacancy-interstitial pairs, has lowest displacement energy out of the graphene plane, although this may be a consequence of the limitations of the potential model used.

In addition, two new models to describe the maximum displacement of a PKA for a given primary knock on energy have been developed. These models are based on energy dependent and momentum dependent homogeneous drag models, and have precedent in the Robinson model for displacement probability, and the NRT model for
the number of displacements as a function of energy. Both the developed models are in good agreement for the simulated data for all materials and PKAs, and as such it is currently not clear which describes the average effect better.

Directional dependence of threshold displacement and defect formation energies in tungsten carbide is somewhat more complicated. For a tungsten PKA, the lowest threshold displacement directions are the \(\langle 2\bar{1}\bar{1}\rangle\) directions, corresponding to carbon nearest neighbours, while the highest are those that cause glancing angle collisions to the tungsten \(\{10\bar{1}0\}\) nearest neighbours. For a carbon PKA, the highest threshold displacement directions are those surrounding the \(\langle 0001\rangle\) directions, while the study used insufficient energy resolution to resolve clear trends across other parts of the stereographic projection. Curiously, this trend is inverted when examining the threshold at which there is a 50% chance of defect formation, where these directions have low threshold energy, and further nearest neighbour tungsten atoms have the highest values. The reason for this remains unexplained, however it is possibly a result of the (more) complex tungsten carbide structure and the presence of strongly directional semi-covalent bonds.

The main practical implications of this work are that the large differences in displacement behaviour between the two interatomic potentials for beryllium, as well as the shortcomings of the potential used to describe graphite, highlight how sensitive displacement behaviour is to the potential used. Potentials must therefore be thoroughly characterised and validated before future displacement or cascade simulations are performed. Further, the strong directional dependence predicted for displacement suggests that when investigating single crystals experimentally, should a tool such as SRIM be used to predict defect populations, this directional dependence should be considered. Finally, significant differences were observed between the threshold displacement ener-
gies of both tungsten and carbon in different structures. This is consistent with the work of Robinson et al. [208] in TiO$_2$, confirming that threshold displacement energy is a function of the local environment of the displaced species and undermines the common approximation that threshold displacement energy is solely species dependent.
Chapter 6

Ongoing and Future Work

6.1 Inelastic Neutron Scattering

Further work should be carried out to better characterise the broadening functions of the Taipan instrument, as the good resolution of the experimental results suggests that at present, the instrument broadening effect has been overestimated. It would be useful to undertake additional studies of materials where no peaks are predicted by DFT simulations in the low energy regime, in order to evaluate whether second order reflections consistently provide better energy resolution than first order. If this is indeed the case, the effect may be used to increase energy resolution in future neutron scattering studies.

To better characterise the $\text{Be}_{12}M$ and $\text{Be}_{13}M$ materials investigated herein, it would also be useful to perform inelastic neutron scattering on single crystal samples in order to observe the phonon dispersion, however the difficulties in obtaining, and working with, single crystals of these materials makes this unlikely. In addition, as DFT is known to have errors of 1-2% in the predicted lattice parameter, it may be possible
to improve correspondence between the DFT and experimental results by scaling the DFT results by the experimental lattice parameter as appropriate.

6.2 Point Defects and Phase Stability in Beryllides

Having investigated point defects and small clusters in Be\(_{12}M\) materials, the next step is to simulate larger clusters, voids and extended defects, in order to better understand the thermodynamics and kinetics of how these defects form. To aid in this, it may also be necessary to develop empirical potentials capable of modelling these systems as DFT is limited to small supercells (<400 atoms). Bjorkas et al. [161] has developed a Be-W potential that provides a reasonable description of Be\(_{12}\)W, however at present it has not been possible to reproduce these results in the LAMMPS code [171]. The development of such potentials would also open the possibility of simulating damage cascades and extended defects.

In the near term, the present defect calculations may be improved upon by using the harmonic and quasiharmonic approximations to calculate the contributions of vibrational enthalpy and entropy to the free energy. This would allow more accurate predictions of properties derived from defect calculations at temperature, which is particularly important for the determination of non-stoichiometry.

The present results may also be used for Monte Carlo transport simulations, particularly for cluster migration. Accelerated dynamics may also be useful to study migration, as it can investigate complex migration mechanisms, which might be difficult to identify conventionally.

In addition to intrinsic defects, an examination of extrinsic defects should also be performed. In particular, the accommodation of radiogenic H and He should be in-
vestigated, although some investigations have already been made in Be$_{12}$Ti [91] and Be$_{12}$W [96]. Many of the common impurities in beryllium [76] would also be expected to be present in Be$_{12}M$ materials, and should be investigated. These include oxygen, iron, uranium, carbon, silicon and aluminium.

Given that Be$_{12}$Mo and Be$_{12}$W have been shown to be unsuitable for neutron multiplying applications from a neutronic perspective, Be$_{22}$W and Be$_{22}$Mo should be considered more fully. This would include point defect calculations and a determination of the degree of nonstoichiometry.

6.3 Threshold Displacement

The work presented in chapter 5 has identified several trends with respect to the spatial dependence of threshold displacement, and the dependence on local environment. It would be useful to test the general applicability of these trends by extending the systematic approach to other materials, for which well characterised empirical potential sets are available. In particular, other BCC and HCP metals may offer useful comparison with tungsten and beryllium respectively, and many have nuclear applications (e.g. iron and zirconium). This may also aid in the models developed for maximum displacement.

It is also planned to extend displacement simulations to higher energies (1 keV-1 MeV) in the materials studied (with the exception of graphite), to test the validity of models due to Kinchin-Pease [225], Norgett-Robinson-Torrens [106] and Greenwood [107]. At these energies, electronic stopping may become significant, therefore the two temperature model should be parameterised and applied.

Finally, it is also envisaged that high energy displacement events will be simulated
repeatedly in single supercells of tungsten, tungsten carbide and diamond, in order to investigate how much energy may be stored in these materials (analogous to Wigner energy in graphite).

Modelling graphite remains a challenge for empirical potentials but also for QM simulations. The work of Telling et al. [226] provides a good starting point to take such work forward.
Bibliography


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