A computational study of surface topography arising from energetic particle interactions

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A computational study of surface topography arising from energetic particle interactions

by

Chris D.J. Scott

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

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Abstract

A computational investigation into the development of surface topographies subjected to energetic particle bombardment has been undertaken. Classical Molecular Dynamics (MD) and on-the-fly kinetic Monte Carlo (otfKMC) techniques were employed and different bombardment conditions were considered. Surface topography development is of interest due to applications such as ion etching, which can be used in the manufacture of semiconductor devices.

Crater formation on a HfO$_2$-MgO interface system was investigated using a variety of methods. Initially single atom and cluster bombardments were performed, highlighting the radiation tolerance of the interface system. Subsequently, swift heavy ion bombardment of the interface was considered using a MD thermal spike model and an electron stripping with recombination model. Both models gave similar results to those seen experimentally: hillocks forming on the surfaces over the impact points of the ions; and ion tracks forming around the paths of the ions in the material. Hillock heights and sputtering yields were shown to increase linearly with the electronic stopping force of the bombarding ion, for the range of systems we considered.

Bullet impacts on armour plating (SiC) have been simulated using MD. The bullet was modelled by a hard sphere that was forced into the substrate to the target depth. Both 4H and 6H SiC polytypes were considered with different bullet sizes and speeds. The 4H system resulted in the displacement of less atoms and also a much lower sputtering yield than for the similar 6H system. However dislocations were seen to propagate through the 4H system but not the 6H one. A large amount of sputtering was observed in the higher speed 6H simulations, with the ejection of many big clusters of atoms. These clusters generally had a high temperature (around 1,500 K) with speeds typically in excess of 1,000 m/s.

Surface topography development by way of multiple impacts on Au was investigated using two different methodologies. Initially a traditional, MD based, methodology was used to model Au self bombardment of the high index \{3 11 0\} surface, which has been shown to produce interesting features. The disadvantage of this type of method is that MD cannot simulate time scales long enough to allow diffusion between impacts. The MD method was shown to lead to a build up of defects in the systems: a result of the artificially high dose rate.

An improved method was then used to model Ar and Au bombardment of both \{0 1 0\} and \{3 11 0\} Au surfaces. This hybrid MD-otfKMC technique enabled realistic time scales to be achieved. MD was used to model the ballistic
phase while otfKMC was used to model diffusion between events. The erosion rate of the surface was shown to be almost linear with time while the roughness of the surface was shown to oscillate: indicative of the healing process that occurs between bombardment events.
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Chapter 1

Introduction and Background

1.1 Introduction

Understanding the development of surface topographies as a result of bombardment by energetic particles has many important applications, including in the semiconductor industry, and for surface analysis and cleaning, to name but a few. The process prevalent during topography development is “sputtering”. This phenomenon, first discovered by Grove in 1852 [1], is the process by which atoms are ejected from the surface of a material subjected to energetic particle bombardment. For large doses (> $10^{17}$ particles/cm$^2$) of energetic ($\gtrsim 10$ keV) particles, changes to the topography can be visible to the naked eye [2]. Sputtering occurs in nature, for example in the erosion of interstellar dust grains [3], and is often characterised by the sputtering yield: the number of target atoms ejected from the surface per incident particle.

Both the erosion and growth of surfaces is of interest. At lower bombardment energies thin film deposition is used in the manufacture of a range of thin films, such as those for use in low emissivity coatings on glass, integrated circuits, optical coatings, and solar panels. A variety of uses also exist at higher energies. Ion etching is a commonly used tool in the manufacture of semiconductor devices [4]. Another use is in sputter-depth profiling
for surface analysis, where techniques such as secondary-ion mass spectroscopy (SIMS) and Auger electron spectroscopy work by characterising the ejected matter or the remaining surface respectively [5].

In the laboratory, topography development is achieved by using one of a variety of methods depending on the desired outcome. The morphology of the surface depends on the energy of the energetic particles bombarding the surface, which varies depending on the technique used. For example, magnetron sputtering uses a plasma and generally deposits atoms in the energy range of 10 eV to 50 eV. This technique is an important technological application, which uses ions to sputter atoms from a target material and deposits them onto a substrate. This is a method by which thin films can be grown on a substrate. At higher energies, a low energy (> 100 eV) ion beam can be used to etch surfaces, a commonly used technique in the manufacture of semiconductor devices.

A special type of sputtering, known as electronic sputtering, occurs when the incoming particle has a very high energy (in the range of MeV to GeV), or when a surface is subjected to bombardment by a highly charged heavy ion. In the former case the stopping force of the particle in the target will be mainly electronic rather than nuclear, and this can result in high sputtering yields. In insulators these ions can leave permanently damaged cylindrical tracks in their wake. These ion tracks have practical applications, for example as templates for the synthesis of micro- and nano-wires and tubes, and textured surfaces and bodies with special optical properties [6, 7]. The process behind the formation of the latent tracks is still under some debate.

1.1.1 Computer simulation

Computer simulation plays an important role in materials science today. As computers have become more and more powerful the models they use have become more accurate, as have the results they obtain. Many different techniques are available depending on what you wish to model and the scales on which you wish to model them. Continuum methods, such as
finite elements, can be used to model situations on larger length and time scales (metres and seconds). At the other end of the scale are ab initio methods, such as density functional theory (DFT) [8], which models on an atomistic level (Å) and very short time scales (up to picoseconds). Classical molecular dynamics (MD) [9, 10] is also an atomistic technique, but can achieve greater length and time scales than ab initio methods, since the forces are derived from interatomic potentials rather than the solution of Schrödinger’s equation.

The first MD computer simulations were carried out in the 1950s when Alder and Wainwright studied phase transitions in a hard sphere system [11]. Vineyard et al were the first to model radiation damage using MD in the 1960s [12]. They used basic pair potential energy functions to model radiation events in systems containing approximately 500 atoms. As computers became more powerful the system sizes that could be modelled grew, as did the complexity of the potential energy functions used to model the materials. It is now possible to model millions of atoms, and reach simulation times of the order of nanoseconds, on typical desktop computers. However this is still some way short of time scales that can be measured experimentally. Hybrid techniques can be used to model even longer time scales. For example MD and on-the-fly kinetic Monte Carlo can be used together to reach simulation times of the order of seconds [13].

In more recent years the development of the Compute Unified Device Architecture (CUDA) [14], by Nvidia, allows computer simulations to run directly on graphics processing units (GPUs). GPUs are massively parallelisable, often with the ability to run thousands of simultaneous threads, and are just starting to be utilised in the area of scientific programming.

1.2 Previous work

The development of surface topographies, and in particular the sputtering process, has been well researched over the years from experimental, theoretical and computational perspectives. As a result the physics of sputtering is reasonably well understood. In this section some of
the previous work in this area is discussed.

1.2.1 Experimental

A large amount of experimental data has been accumulated over the years on energetic particle bombardment. Particularly measurements such as sputtering yields for different particle energies and materials, and also the angular and energy distributions of sputtered atoms. In the 1950s Wehner carried out experiments on different crystal structures and showed the angular dependence of the sputtered atoms on the structure of the target material [15]. A large amount of data on the sputtering yields of different materials, for different impacting particle species, and different particle energies can be found in the text edited by Behrisch [16].

Carter et al showed the dramatic changes that can occur to surface topographies under bombardment in their experimental work on bombarding a copper target [17, 18]. The authors bombarded \( \{11 \overline{3} 1\} \)-oriented copper targets with high fluences (\( \geq 10^{19} \) per cm\(^2\)) of 40 keV projectiles of differing species, ranging from light to heavy. They found that all ion species lead to large changes in the surface topography, with etch pits and pyramids forming, as a result of sputtering.

In recent years there has been a lot of experimental research done on the subject of swift heavy ion bombardment of surfaces (for example [19, 20, 21]). These studies show interesting surface topographies developing as a result of the bombardment, with hillocks forming over the impact points of the heavy ions on the surface. The formation of these hillocks and of the defective track regions in the material are an area of intense interest.

Other authors have investigated ripple patterns that form on semiconductors (specifically Si) subjected to ion bombardment at oblique incidences [22, 23]. The formation of well ordered ripple patterns is observed. As fluence increases so does the length and wavelength of the ripples.

To conclude, a wide variety of structures and patterns have been observed to form on
surfaces, as a result of energetic particle bombardment, experimentally. In the next section some of the theoretical models that have been developed to explain the formation of these structures are discussed.

1.2.2 Theoretical

Boltzmann transport models

In the 1960s Sigmund and Thompson developed their analytical approaches to describing the sputtering process. Using Boltzmann transport theory they calculated the sputtering yield and energy distributions of sputtered atoms following bombardment of a random target [24, 25]. Sigmund’s model, generally thought of as the most complete analytical theory of sputtering [26], outlines the following process for sputtering:

- Initially the impacting ion undergoes a series of binary collisions in the target.

- Atoms that recoil with sufficient energy undergo secondary collisions, and so on. Atoms ejected during this phase form only a minor portion of the sputter yield but constitute the bulk of the sputtered energy.

- Slowing down paths of recoil atoms are surrounded by higher order recoil atoms with very low energy. These higher order recoil atoms have short ranges of motion so are only sputtered if they are close to the surface, but there are many of them so they account for the bulk of the sputter yield.

Boltzmann transport models predict general trends quite well, such as the effect the energy of the bombarding specie has on the sputtering yield, but are less useful when modelling crystalline materials [2]. The general conclusion from these theoretical calculations is that the kinetic energy distribution of the sputtered particles peaks at around half the cohesive energy of the target material.
Swift heavy ions

A number of different theoretical models have been proposed for modelling swift heavy ion bombardment of a material, such as the Coulomb explosion and thermal spike models. Szenes has used his thermal spike model to investigate ion track formation in insulators [27, 28]. The basic assumption behind all thermal spike models is that a high temperature region forms around the path of the ion through the material, causing the material to melt (for sufficiently high energy ions). Due to the small diameter of the spike region the cooling rate can be very high, reaching $10^{13}$ to $10^{14}$ K/s [27]. This high cooling rate can result in an amorphous phase forming when the spike region cools.

Surface topography theory

Surface topography development has been investigated using a non-linear wave formalism [29, 30]. These models could explain the formation of cones, pyramids and pits on surfaces with an initial impurity, and later on pure crystals too. However they could not model some ripple formations and other features that occur under large fluences. Bradley and Harper developed a theory of ripple topography development on a surface subjected to ion bombardment [31]. They perform a linear stability analysis of a surface roughening due to sputtering and healing by surface diffusion.

1.2.3 Computational

At around the same time as the early transport theory models started to appear, work also began on modelling sputtering using computational techniques. Use of computer simulation can help explain processes that are not accessible by experiment due to them happening on too small a length or time scale. Computational work on sputtering and the development of topographies can generally be split into two sections: one that uses the binary collision approximation and the other that uses MD simulation.
1.2. PREVIOUS WORK

Figure 1.1: Illustration of a cascade using the binary collision approximation. The darker solid line represents the surface of the material while the lighter solid lines represent the trajectories of atoms. The purple circle is the incoming projectile. Red circles are secondary atoms, blue tertiary, and so on. Taken from [32].

Binary collision approximation

The method of studying surface topographies and sputtering using the binary collision approximation (BCA) descended from the transport theory techniques already discussed. It is assumed that particles interact in a pairwise fashion, i.e. an atom travelling through a material can only hit one other atom at a time. Trajectories of atoms between impacts are assumed to be straight lines and the influence of neighbouring atoms is neglected. An example of a collision cascade using this approximation is shown in Figure 1.1. The advantage of codes using the BCA is that they are fast and therefore allow good statistics to be obtained. However the BCA does not always hold, especially at lower energies (≲ 1 keV) where many body effects become dominant [33, 34]. BCA codes can generally be divided into two groups: lattice BCA codes used to simulate a crystalline target; and Monte Carlo (MC) BCA codes used to simulate an amorphous target. An example of the former type is MARLOWE [35], while TRIM [36] is a popular MC BCA code. Since the interactions between particles in these models are usually purely repulsive an input to a simulation is the surface binding energy, $U_0$, which acts as a barrier to atoms in the material. If a particle arrives at this barrier with energy $E$ at an angle of incidence $\theta$ it will leave the barrier with energy $E'$ and
direction $\theta'$:

$$E' = E - U_0,$$  \hspace{1cm} (1.1)

$$\cos \theta' = \left( \frac{E \cos^2 \theta - U_0}{E'} \right)^{\frac{1}{2}}.$$  \hspace{1cm} (1.2)

Thus if a particles energy is less than $U_0$ it will be reflected back into the material. BCA codes have been used extensively in the determination of sputtering yields [37] and to predict the spectra observed in ion scattering spectroscopy [2].

**Molecular dynamics**

Molecular dynamics (MD) is the other popular computational tool used to investigate the sputtering process. MD implicitly accounts for many body interactions and so can be used to model lower energy particle bombardment. However an MD simulation is much more time consuming than those using the BCA.

Harrison pioneered the use of MD for modelling sputtering in the 1960s [38]. Using purely repulsive pair potentials he produced spot patterns similar to those found experimentally by Wehner, and later showed the channelling and blocking mechanisms by surface atoms that were responsible for the emission patterns of crystals [39]. Following his simulations Harrison classified three broad regimes for the final state of the system: low yield trajectories that occur regularly when the ion channels into the lattice; average yield trajectories that occur when an ion with energy in the low keV range transfers most of its energy to one primary knock-on atom (PKA); and high yield trajectories where the ion makes several hard impacts in the top layers of the target.

In the 1980s more advanced, many body potential energy functions were developed, allowing for more accurate MD simulations of surface topography development and sputtering. The work by Garrison et al [40], where the authors performed a large number of single particle impacts on perfect crystals, also predicted that channelling and blocking by surface atoms was responsible for the sharp features on the angular ejection patterns of crystals.
The authors showed that using a many-body potential improved the agreement between their calculated and the experimental results, compared to previous work using a pairwise potential.

Swift heavy ion bombardment has also been modelled using MD. Itoh et al summarise models for the creation of swift heavy ion tracks [41], including thermal spike and Coulomb explosion models. Bringa et al performed MD simulations to investigate electronic sputtering, using a thermal spike model and a Coulomb explosion model [42, 43]. They identify three sputtering regimes. For low electronic energy losses the sputtering yield is linear with the stopping force. As the stopping force gets bigger the yield becomes non-linear but then, for a fixed track radius, the yield becomes linear again. Pakarinen et al use MD to investigate track structure using a thermal spike model [44]. They find that the damage in their system forms in a well defined region around the path of the ion. The authors describe three key factors determining track formation: the local temperature must exceed the melting point of the material; material transfer (atoms forced out of the track region due to a pressure wave caused by the bombarding ion, and then flowing back to the track region); and recrystallisation of the material competing with very high cooling rates in the molten track.

Duffy et al have created a model that couples an atomistic (MD) simulation with an electronic energy model by means of the heat diffusion equation and Langevin thermostat [45]. This model has been used to investigate the formation of swift heavy ion tracks in metals [41, 46]. The advantages of this model are it allows you to see the extent of the core melting and also to calculate the residual defect configurations.

1.3 Thesis structure and aims

The aim of this thesis is to model surface topography development on an atomistic level under different bombardment conditions. This chapter has provided a setting for the work that will
be done. In the following chapter the methodology that will be employed will be described in detail. In the first of the results chapters MD computer simulation will be used to model swift heavy ion bombardment in an attempt to better understand specific experimental results in the area. In the following chapter particle impacts at much lower energies are investigated, specifically bullet impacts on armour plating. The final two chapters focus on the modelling of surface erosion due to low energy ion bombardment. The first of these chapters uses a traditional, MD based, technique for modelling multiple particle impacts. In the final chapter an improved method is used, which allows for more realistic time scales to be achieved during the simulation.
Chapter 2

Methodology

2.1 Molecular dynamics

2.1.1 Introduction

Molecular dynamics (MD) is an atomistic computer simulation technique that uses classical mechanics to follow the time evolution of a system of interacting particles. Ideally a system of atoms would be evolved by integrating Schrödinger’s equation. However, due to its complexity, this is only realistically achievable for systems containing small numbers of atoms. By treating the atoms in the system as point particles and approximating their motion with Newton’s equations of motion, MD can simulate millions of atoms over time scales of the order of nanoseconds to microseconds. The length scales generally accessible by MD are of the order of nanometres, although by linking MD simulations to continuum models these length scales can be increased to those seen experimentally [47]. MD was first used by Alder and Wainwright [11] in the 1950s, and has since been used for many different applications including radiation effects [48, 49], sputtering [43, 50, 51] and the study of biological molecules [52, 53]. The MD code utilised in this work was the LBOMD (LoughBOrough Molecular Dynamics) package. This section will outline the aspects of MD used, and their implementation, in this thesis.
2.1.2 Time evolution

In order to obtain the trajectories of the $N$ particles in the simulation a time integration algorithm is required to numerically solve the equations of motion:

$$F_i = m_i \ddot{r}_i, \quad i = 1, \ldots, N,$$

(2.1)

where $r_i$ is the position of atom $i$ and $\ddot{r}_i$ its acceleration, $m_i$ is its mass and $F_i$ is the force acting upon the atom. Normally $F_i$ is calculated from the gradient of the potential energy function, $V$ (discussed in the next section), with respect to the atoms position:

$$F_i = -\nabla_{r_i} V.$$

(2.2)

Correct choice of the numerical integrator is essential, with desirable properties including: the ability to choose a large time step; require as few force evaluations as possible; duplicate the classical trajectory as closely as possible; conserve energy and momentum; and be time reversible [54]. In order to ensure the conservation of energy over long time scales a symplectic integrator is best employed. This rules out many common algorithms such as the Runge-Kutta method. Multi-step methods are also generally avoided since they work best with a fixed time step, whereas MD programmes tend to use variable time steps. If a particle has a high kinetic or potential energy then a smaller time step is required for a given accuracy [2]. Conversely, if a system is near equilibrium and the forces are small, there is no need to use a small time step.

The time integration algorithm utilised by the LBOMD programme is the second order Velocity Verlet algorithm [55]:

$$r_i(t + \delta t) = r_i(t) + \delta t \dot{r}_i(t) + \frac{1}{2m_i} \delta t^2 F_i(t) \quad (2.3)$$

$$\dot{r}_i(t + \delta t) = \dot{r}_i(t) + \frac{1}{2m_i} \delta t [F_i(t) + F_i(t + \delta t)], \quad (2.4)$$
where $t$ is time, $\delta t$ the time step, $m_i$ the mass of particle $i$ and $\dot{r}_i$ its velocity. This method, developed from the earlier algorithm first used by Verlet [56], stores positions, velocities and accelerations for the same time $t$, and minimises round-off error [54].

A variable time step is used by the LBOMD programme that depends on the maximum kinetic energy and the maximum positive potential energy:

$$\delta t = \frac{1.5}{\sqrt{1.5 + 0.1T_s}}, \quad (2.5)$$

where $T_s$ is the sum of the maximum kinetic energy and maximum positive potential energy (zero if all negative) in the system. A typical time step is 1 fs ($1 \times 10^{-15}$ s), after the ballistic phase of a collision cascade.

### 2.1.3 Potential energy function

At the heart of a MD programme is the interatomic potential energy function, $V(r_1, \ldots, r_N)$, depending on the positions $r_1, \ldots, r_N$ of the $N$ atoms in the system. In its general form the interatomic potential energy function is a series of summations over increasing numbers of atoms [57]:

$$V_{TOT} = \sum_{i,j} V_2(r_i, r_j) + \sum_{i,j,k} V_3(r_i, r_j, r_k) + \ldots, \quad (2.6)$$

where $V_2$ is the interaction between pairs of atoms $\{i, j\}$, $V_3$ the interaction between triplets of atoms $\{i, j, k\}$, and so on. In its simplest form Equation 2.6 becomes a pair potential depending only on the internuclear separation, $r_{ij} = ||r_j - r_i||$, of atoms $i$ and $j$ as shown in the following equation:

$$V_{TOT} \approx \sum_{j > i} V_2(r_{ij}). \quad (2.7)$$

Although this pair potential model does have some shortcomings, for example when modelling metals [58, 59], it is well established in the modelling of ionic systems where electrostatics dominate [60]. The advantage of this form of potential energy function is the ease
with which it can be implemented and its speed of execution, due to its simplicity. Note the sum in Equation 2.7 is over \( j > i \) since \( V_2 \) is symmetric with respect to the ordering of atoms \( i \) and \( j \), thus their interaction need only be calculated once. Pair potentials have been used successfully in numerous studies investigating radiation damage in ionic materials [48, 49, 61]. In the case of ionic materials the pair potential function can be further broken down into a long ranged component, \( V_{LR} \), and a short ranged component, \( V_{SR} \) [62]:

\[
V_2(r_{ij}) = V_{SR}(r_{ij}) + V_{LR}(r_{ij}).
\]  

(2.8)

The long ranged component is the Coulombic interaction and accounts for the bulk of the cohesive energy in the system. The short range part is mainly repulsive, ensuring that atoms are not able to pass through one another, although it may also contain an attractive element, for example to model dipole interactions at intermediate distances.

The need to accurately model more complex situations, for example metals and intricate formations such as cracks, led to the development of more advanced potential energy functions than the pairwise additive variety. In the 1980s potentials for metals were developed which consisted of a pair part and a many-body part. The many-body part takes into account the coordination number or local density of particles and is based on the idea of the Drude model of metals [63], where atoms are embedded in a sea of electrons, and the idea that bonds are weaker the higher the local density of particles [64]. Examples of such potentials are the embedded atom method (EAM) [58] of Daw and Baskes, and the Finnis-Sinclair potential [65]. Semiconductors, such as silicon, require even more complicated potentials depending on coordination number, bond angle and bond order.

Once a suitable form for the potential energy function is found the potential is usually parameterised via some form of empirical fitting, i.e. until it gives the best possible fit to as much data as possible (lattice constants, elastic constants, bulk modulus, melting point, etc.). This data can be obtained from experimental work or from more accurate calculations
such as density functional theory [66].

**Buckingham potential**

At short ranges a repulsive potential is required to stop atoms from passing through one another. An early proposed model was that of Born and Mayer [67]:

$$V_{BM}(r_{ij}) = A_{ij} \exp \left( -\frac{r_{ij}}{\rho_{ij}} \right),$$  \hspace{1cm} (2.9)

where the parameters $A_{ij}$ and $\rho_{ij}$ depend on the species of atoms $i$ and $j$. This model represents the Pauli repulsion. Buckingham added an attractive van der Waal’s dipole potential element to the Born-Mayer potential to give us the Buckingham pair potential [68]:

$$V_B(r_{ij}) = A_{ij} \exp \left( -\frac{r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6},$$  \hspace{1cm} (2.10)

where the additional parameter $C_{ij}$ also depends on the species of atoms $i$ and $j$. The Buckingham potential has been widely used to model ionic solids [62, 69] and was used throughout Chapter 3 of this thesis. Specific detail of the form of the potential energy function is discussed in a later section.

**Lennard-Jones potential**

Another simple pair potential is the Lennard-Jones potential [70] which has been used extensively in modelling the noble gases. One form of this potential is given in the following equation:

$$V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right],$$  \hspace{1cm} (2.11)

where $\sigma$ and $\epsilon$ are material dependent parameters measuring the strength of attraction and the radius of the repulsive core [71]. This potential was used to model Ar-Ar interactions in this thesis.
Ziegler-Biersack-Littmark (ZBL) potential

A short range potential, such as the Buckingham potential, should be sufficient to model the short range interaction from Equation 2.8 if only low energy cascades were to be performed. However since higher energy cascades will be simulated in this work it is essential to utilise a more accurate potential at small particle separations.

When the internuclear separation between two atoms becomes very small their interaction is dominated by the repulsion between the nuclei and not by the outer electrons. As their separation increases the cores of the atoms become screened by the electron cloud, reducing the repulsion. The ZBL universal repulsive potential \[72\] of Ziegler, Biersack and Littmark models this close range interaction by multiplying the Coulombic potential between the atom cores by a screening function. The ZBL potential is widely used and has been shown to have very good accuracy \[2, 57, 73\]. The ZBL potential has the form:

\[
V_{ZBL}(r_{ij}) = \frac{e^2}{4\pi\epsilon_0} \frac{Z_1 Z_2}{r_{ij}} \phi(r_{ij}),
\]

(2.12)

where \(Z_1\) and \(Z_2\) are the atomic numbers of atoms \(i\) and \(j\), \(\epsilon_0\) is the permittivity of free space and \(e\) is the charge of an electron. The screening function \(\phi\), constructed using the quantum mechanical Thomas-Fermi approximation, has the form:

\[
\phi(x) = 0.1818e^{-3.1998x} + 0.5099e^{-0.9423x} + 0.2802e^{-0.4029x} + 0.02817e^{-0.2016x},
\]

(2.13)

where \(x = \frac{r_{ij}}{a_u}\) and \(a_u\) is given by:

\[
a_u = \frac{0.8854a_0}{Z_1^{0.23} + Z_2^{0.23}},
\]

(2.14)

where \(a_0\) is the Bohr radius.
2.1. MOLECULAR DYNAMICS

Figure 2.1: The splining function (yellow) matching the Buckingham potential (green) to the close range ZBL potential (red). The spline function is in effect between 0.4 and 1.0 Å.

Spline function

Since many of the potential energy functions used in this work are piecewise functions consisting of a very short ranged ZBL potential linked to another short range potential, for example the Buckingham potential, we require a method to match these potentials to each other. In order to ensure the conservation of energy throughout the simulation the potentials are splined together using a fifth order exponential splining function, \( g \), of the form:

\[
g(r_{ij}) = \exp \left( f_0 + f_1 r_{ij} + f_2 r_{ij}^2 + f_3 r_{ij}^3 + f_4 r_{ij}^4 + f_5 r_{ij}^5 \right),
\]

where the coefficients \( f_0, \ldots, f_5 \) were calculated so as to make the function and its first and second derivatives smooth and continuous. An example of the splining function is shown in Figure 2.1 where the spline occurs between 0.4 and 1.0 Å.

In the case of the short-ranged potentials (i.e. not electrostatic) we apply a final cutoff distance beyond which the potential is no longer evaluated. It is essential that this cutoff is also smooth and continuous, which is achieved by using the following cosine screening
function:
\[ h(r_{ij}) = \frac{1}{2} \left( 1 + \cos \pi \frac{r_{ij} - r_c}{D} \right), \]  \hspace{1cm} (2.16)
where \( r_c \) is the cutoff distance and \( D \) is the range over which the potential is attenuated. We make use of this function with the Buckingham and Lennard-Jones potentials, whereas the Ackland and Tersoff potentials (discussed later) handle this smooth attenuation implicitly.

**Coulomb potential**

In ionic materials the electrostatic forces between charged particles must also be considered. The Coulomb potential forms the long ranged component of Equation 2.8 and describes the interaction between two charged particles. It is directly proportional to the size of the charges and inversely proportional to their separation \( r_{ij} \):

\[ V_C (r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}, \]  \hspace{1cm} (2.17)
where \( q_i \) and \( q_j \) are the charges on atoms \( i \) and \( j \), and \( \epsilon_0 \) is the permittivity of free space. When both charges have the same sign \( V_C \) will be repulsive, whereas if the signs differ \( V_C \) will be attractive. The Coulomb potential is a long ranged potential since it decays slowly as internuclear separation increases. This means it is much more time consuming to calculate than shorter range potentials and is therefore calculated separately. This will be discussed in a later section.

**Ackland potential**

Ackland et al developed their many-body potential [74] based on the earlier EAM and Finnis-Sinclair type potentials [58, 65]. The idea behind these techniques is that an atom is embedded in a sea of electrons, as discussed earlier. The energy associated with the embedding of the atom in the sea is dependent on the electron density surrounding the atom. The electron density can be thought of as atomic density and depends on the internuclear
2.1. MOLECULAR DYNAMICS

<table>
<thead>
<tr>
<th>k</th>
<th>$a_k$ (eV)</th>
<th>$r_k$ (Å)</th>
<th>$(r_k/r_L)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.059</td>
<td>4.995</td>
<td>3/2</td>
</tr>
<tr>
<td>2</td>
<td>-153.148</td>
<td>4.709</td>
<td>4/3</td>
</tr>
<tr>
<td>3</td>
<td>148.179</td>
<td>4.559</td>
<td>5/4</td>
</tr>
<tr>
<td>4</td>
<td>-22.205</td>
<td>4.078</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>72.715</td>
<td>3.532</td>
<td>3/4</td>
</tr>
<tr>
<td>6</td>
<td>199.263</td>
<td>2.884</td>
<td>1/2</td>
</tr>
</tbody>
</table>

Table 2.1: Au-Au Ackland parameters for $V_2$ (Equation 2.19).

<table>
<thead>
<tr>
<th>k</th>
<th>$A_k$ (eV$^2$)</th>
<th>$R_k$ (Å)</th>
<th>$(R_k/r_L)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.930</td>
<td>4.559</td>
<td>5/4</td>
</tr>
<tr>
<td>2</td>
<td>284.996</td>
<td>3.532</td>
<td>3/2</td>
</tr>
</tbody>
</table>

Table 2.2: Au-Au Ackland parameters for $\phi$ (Equation 2.21).

separation to neighbouring atoms. The form of the Ackland potential is given in the following equation:

$$V_{ACK} = \sum_{j>i} V_2(r_{ij}) + \sum_i F_i \left( \sum_{j>i} \phi_{ij}(r_{ij}) \right), \quad (2.18)$$

where $V_2$ is the pairwise interaction between atoms $i$ and $j$, $\phi_{ij}$ represents the contribution of atom $j$ to the density of the electron field around atom $i$, and $F_i$ is the embedding energy of atom $i$ depending on the density of the surrounding electron field. These functions have the following general forms:

$$V_2(r) = \sum_k a_k (r_k - r)^3 H(r_k - r), \quad (2.19)$$

$$F(\rho) = -\sqrt{\rho} + c_2 \rho^2 + c_4 \rho^4, \quad (2.20)$$

$$\phi(r) = \sum_k A_k (R_k - r)^3 H(R_k - r), \quad (2.21)$$

<table>
<thead>
<tr>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$f_0$</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>$f_3$</th>
<th>$f_4$</th>
<th>$f_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>2.0</td>
<td>29.760816</td>
<td>-81.916249</td>
<td>122.474139</td>
<td>-93.756723</td>
<td>34.430181</td>
<td>-4.835077</td>
</tr>
</tbody>
</table>

Table 2.3: Parameters for the spline function, $g$, matching the ZBL potential to the Ackland potential for the Au-Au interaction. The $f_k$’s are in units $Å^{-k}$. $C_1$ and $C_2$ are in units of $Å$. 
where $H$ is the Heaviside step function and the parameters $A_k$, $a_k$, $R_k$ and $r_k$ depend on the species of atoms $i$ and $j$ ($i,j$ subscripts omitted for clarity). In this thesis we use the Ackland potential to model Au-Au interactions and take the parameters $c_2 = c_4 = 0$, resulting in the embedding function $F(\rho) = -\sqrt{\rho}$. The Au parameters are taken from [74] and are shown in Tables 2.1 and 2.2, where the Au lattice parameter $r_L = 4.078$ Å. To ensure realistic behaviour at small particle separations we made use of the ZBL universal repulsive potential. This potential was matched to the pairwise component of the Ackland potential using a fifth order exponential spline function, the form of which has already been discussed. The spline parameters and associated cut-off distances are shown in Table 2.3. For separations less than $C_1$ we replace $V_2$ from Equation 2.19 with the ZBL potential. Between $C_1$ and $C_2$ we use the spline function and at separations greater than $C_2$ we return to the normal form of $V_2$. At separations greater than $C_3$, where $C_3$ is equal to the greatest of the $R_k$ and $r_k$ values, the potential is equal to zero and does not need to be evaluated.

The many-body component is calculated for all separations less than $C_3$. An advantage of the Ackland potential is that, although it includes a many-body term, it requires no 3-body loops and as such is only a factor of roughly 2 slower than pure pairwise potentials [57].

Table 2.4: Tersoff potential parameters for Si and C, taken from [75].

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ (eV)</td>
<td>$1.3936 \times 10^4$</td>
<td>$1.8308 \times 10^4$</td>
</tr>
<tr>
<td>$B$ (eV)</td>
<td>$3.467 \times 10^2$</td>
<td>$4.7118 \times 10^2$</td>
</tr>
<tr>
<td>$\lambda$ ($\text{Å}^{-1}$)</td>
<td>$3.4879$</td>
<td>$2.4799$</td>
</tr>
<tr>
<td>$\mu$ ($\text{Å}^{-1}$)</td>
<td>$2.2119$</td>
<td>$1.7322$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$1.5724 \times 10^{-7}$</td>
<td>$1.1 \times 10^{-6}$</td>
</tr>
<tr>
<td>$n$</td>
<td>$7.2751 \times 10^{-1}$</td>
<td>$7.8734 \times 10^{-1}$</td>
</tr>
<tr>
<td>$c$</td>
<td>$3.8049 \times 10^4$</td>
<td>$1.0039 \times 10^5$</td>
</tr>
<tr>
<td>$d$</td>
<td>$4.384 \times 10^0$</td>
<td>$1.6217 \times 10^1$</td>
</tr>
<tr>
<td>$h$</td>
<td>$-5.7058 \times 10^{-1}$</td>
<td>$-5.9825 \times 10^{-1}$</td>
</tr>
<tr>
<td>$R$ (Å)</td>
<td>1.8</td>
<td>2.7</td>
</tr>
<tr>
<td>$S$ (Å)</td>
<td>2.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>
2.1. MOLECULAR DYNAMICS

Tersoff potential

As already mentioned, in order to accurately model covalent materials, such as Si, we need a more complex potential that depends on coordination number and bond order, thus requiring an additional 3-body term. One such potential is the Tersoff potential [76], improved in [75], that was specifically designed to model covalent Si and C systems. In his later paper Tersoff considers only cubic SiC but notes that, due to the short range nature of the potential, there is no difference in energy between the cubic and hexagonal polytypes, since they have identical nearest neighbour arrangements. The Tersoff potential energy function is given in the following equation:

\[ V_{TOT} = f_C(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})], \]  

(2.22)

where \( f_R \) is a repulsive potential similar to that of Born and Mayer, \( f_A \) is an attractive component associated with bonding, and \( b_{ij} \) is a measure of bond order containing a 3-body term. The cutoff function, \( f_C \), limits the range of the potential in a smooth manner, ensuring computational efficiency. These functions are given in the following equations:

\[
f_C(r_{ij}) = \begin{cases} 
1 & \text{if } r_{ij} \leq R_{ij} \\
\frac{1}{2} + \frac{1}{2} \cos \left[ \frac{\pi (r_{ij} - R_{ij})}{S_{ij} - R_{ij}} \right] & \text{if } R_{ij} < r_{ij} < S_{ij} \\
0 & \text{if } r_{ij} \geq S_{ij},
\end{cases}
\]  

(2.23)

\[
f_R(r_{ij}) = A_{ij} \exp (-\lambda_{ij} r_{ij}),
\]  

(2.24)

\[
f_A(r_{ij}) = -B_{ij} \exp (-\mu_{ij} r_{ij}),
\]  

(2.25)

\[
b_{ij} = \chi_{ij}(1 + \beta_i \zeta_{ij})^{-1/2n_i},
\]  

(2.26)

\[
\zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}) \omega_{ik} \left( 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos \theta_{ijk})^2} \right),
\]  

(2.27)

where \( \lambda_{ij} = (\lambda_i + \lambda_j)/2 \) and \( \mu_{ij} = (\mu_i + \mu_j)/2 \). Parameters \( A_{ij}, B_{ij}, R_{ij} \) and \( S_{ij} \) are given by \( x_{ij} = \sqrt{x_i x_j} \) for \( x = A, B, R, S \). As usual, \( r_{ij} \) is the internuclear separation (or bond length)
between atoms \( i \) and \( j \), and \( \theta_{ijk} \) is the bond angle between the \( ij \) and \( ik \) bonds. Thus the only remaining parameters that need to be defined are the single element parameters for Si and C, plus \( \omega_{SiC} = 1 \) and \( \chi_{SiC} = 0.9776 \) (\( \omega_{ij} = \chi_{ij} = 1 \) when \( i = j \)). These remaining parameters are given in Table 2.4.

### 2.1.4 Generic pair potential module

For the purposes of this thesis a universal pair potential module was written and integrated into the LBOMD code. The module was able to work alongside the other potential modules already incorporated in the LBOMD programme and could handle Lennard-Jones, Buckingham and ZBL screened Coulomb potentials. In the case of Lennard-Jones and Buckingham potentials, a ZBL potential was also incorporated at short range to ensure realistic behaviour was observed at very close particle separations. If required the module would also call the

<table>
<thead>
<tr>
<th>Type</th>
<th>( R_1 ) (( \text{Å} ))</th>
<th>( R_2 ) (( \text{Å} ))</th>
<th>( R_3 ) (( \text{Å} ))</th>
<th>( \epsilon ) (eV)</th>
<th>( \sigma ) (( \text{Å} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>0.5</td>
<td>1.05</td>
<td>7.4</td>
<td>22764.0</td>
<td>0.149</td>
</tr>
<tr>
<td>Hf-O</td>
<td>0.3</td>
<td>0.9</td>
<td>7.4</td>
<td>1492.6</td>
<td>0.3478</td>
</tr>
<tr>
<td>Mg-O</td>
<td>0.3</td>
<td>0.8</td>
<td>7.4</td>
<td>1428.5</td>
<td>0.2945</td>
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<tr>
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<td>0.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg-Mg</td>
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<td>1.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O-Ar</td>
<td>0.5</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hf-Ar</td>
<td>0.5</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg-Ar</td>
<td>0.5</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O-Au</td>
<td>0.5</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hf-Au</td>
<td>0.5</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg-Au</td>
<td>0.5</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ar-Au</td>
<td>0.5</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ar-Si</td>
<td>0.7</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ar-C</td>
<td>0.7</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.5: Buckingham and ZBL potential parameters used in this thesis. Potentials of type \( V_B \) are Buckingham potentials of the form shown in Equation 2.28, while those of type \( V_Z \) are ZBL potentials as shown in Equation 2.29.

<table>
<thead>
<tr>
<th>( \text{Ar-Ar} )</th>
<th>( R_1 ) (( \text{Å} ))</th>
<th>( R_2 ) (( \text{Å} ))</th>
<th>( R_3 ) (( \text{Å} ))</th>
<th>( \epsilon ) (eV)</th>
<th>( \sigma ) (( \text{Å} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-Ar</td>
<td>2.1</td>
<td>3.0</td>
<td>7.4</td>
<td>0.0104</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 2.6: Lennard-Jones potential parameters used in this thesis. Parameters taken from [71].
2.1. MOLECULAR DYNAMICS

Table 2.7: Parameters (to 6 decimal places) for the splining functions used with the Buckingham, Lennard-Jones and ZBL potentials shown in Tables 2.5 and 2.6. The \( f_k \)'s are in units Å\(^{-k} \).

<table>
<thead>
<tr>
<th></th>
<th>( f_0 )</th>
<th>( f_1 )</th>
<th>( f_2 )</th>
<th>( f_3 )</th>
<th>( f_4 )</th>
<th>( f_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>-0.913836</td>
<td>64.440733</td>
<td>-209.567623</td>
<td>295.900189</td>
<td>-194.812649</td>
<td>49.001910</td>
</tr>
<tr>
<td>Hf-O</td>
<td>16.182725</td>
<td>-68.498425</td>
<td>254.218104</td>
<td>-499.559635</td>
<td>455.147367</td>
<td>-153.510546</td>
</tr>
<tr>
<td>Mg-O</td>
<td>13.738849</td>
<td>-60.637849</td>
<td>233.159119</td>
<td>-491.187979</td>
<td>499.111027</td>
<td>-196.189385</td>
</tr>
<tr>
<td>Hf-Mg</td>
<td>16.408130</td>
<td>-55.788478</td>
<td>160.299378</td>
<td>-477.205360</td>
<td>529.081435</td>
<td>-210.804175</td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>14.450075</td>
<td>-47.792783</td>
<td>122.405778</td>
<td>-175.977754</td>
<td>125.115142</td>
<td>-34.143959</td>
</tr>
<tr>
<td>O-Ar</td>
<td>9.954239</td>
<td>-11.670431</td>
<td>9.487373</td>
<td>-4.144358</td>
<td>0.981418</td>
<td>-0.099878</td>
</tr>
<tr>
<td>Hf-Ar</td>
<td>14.856989</td>
<td>-33.130178</td>
<td>66.001658</td>
<td>-76.085704</td>
<td>41.900948</td>
<td>-8.571223</td>
</tr>
<tr>
<td>Mg-Ar</td>
<td>11.518679</td>
<td>-20.342042</td>
<td>32.813782</td>
<td>-33.920359</td>
<td>18.071776</td>
<td>-3.678256</td>
</tr>
<tr>
<td>Hf-Au</td>
<td>18.105589</td>
<td>-47.129778</td>
<td>102.556590</td>
<td>-121.488781</td>
<td>67.082100</td>
<td>-13.673050</td>
</tr>
<tr>
<td>Ar-Au</td>
<td>14.324292</td>
<td>-17.494625</td>
<td>12.724469</td>
<td>-5.138375</td>
<td>1.148808</td>
<td>-0.110509</td>
</tr>
<tr>
<td>Ar-C</td>
<td>11.670788</td>
<td>-21.859312</td>
<td>29.43306</td>
<td>-23.192872</td>
<td>8.578897</td>
<td>-1.163832</td>
</tr>
<tr>
<td>Ar-Ar</td>
<td>-107.097071</td>
<td>249.099790</td>
<td>-220.139775</td>
<td>94.646510</td>
<td>-19.931924</td>
<td>1.639312</td>
</tr>
</tbody>
</table>

The appropriate routine to evaluate electrostatics (discussed later).

The form of the potential energy function, \( V_U \), used when either a Buckingham or Lennard-Jones potential was required is given in the following equation:

\[
V_U = \begin{cases} 
V_{ZBL} & \text{if } r_{ij} < R_1 \\
g & \text{if } R_1 \leq r_{ij} < R_2 \\
V_{SR} + V_{LR} & \text{if } R_2 \leq r_{ij} < R_3 - D \\
h \times V_{SR} + V_{LR} & \text{if } R_3 - D \leq r_{ij} < R_3 \\
V_{LR} & \text{if } r_{ij} \geq R_3,
\end{cases}
\tag{2.28}
\]

where \( r_{ij} \) is the internuclear separation between atoms \( i \) and \( j \), \( g \) is the exponential spline function and \( h \) is a cosine switching function used to smoothly attenuate \( V_{SR} \) over a distance \( D \) (taken to be 0.2 Å in all cases). \( V_{SR} \) is the Buckingham or Lennard-Jones short-ranged potential, \( V_{LR} \) is the long-ranged Coulombic potential and \( V_{ZBL} \) is the ZBL potential. In non-ionic systems \( V_{LR} = 0 \). When only a repulsive ZBL potential was required \( V_U \) takes the
following form:

\[ V_U = \begin{cases} 
V_{ZBL} & \text{if } r_{ij} < R_1 \\
g & \text{if } R_1 \leq r_{ij} < R_2 \\
V_{LR} & \text{if } r_{ij} \geq R_2.
\end{cases} \]  

Thus the parameters that are required to define interactions in this generic module are:

- Atomic numbers and charges of both species;
- Buckingham or Lennard-Jones parameters (unless ZBL only);
- Cut-offs – \( R_1, R_2, R_3 \);
- Spline parameters – \( f_0, \ldots, f_5 \) and \( S \);

where \( S \geq 0 \) was a constant added to \( V_U \) during splining to ensure the spline points were greater than 0. These parameters are placed in an input file which is read at the beginning of the simulation, with the values used in this work shown in Tables 2.5, 2.6 and 2.7.

### 2.1.5 Optimisation

#### Neighbour lists

All the potential energy functions discussed earlier, apart from the Coulomb potential, decay rapidly as interatomic separation increases. Furthermore, most of these potentials are truncated to zero outside some cutoff range, \( r_c \). Thus it would be inefficient to calculate the interaction of each atom with every other atom in the system, an \( \mathcal{O}(N^2) \) operation where \( N \) is the number of particles in the system. Rather it is possible to create and maintain a list of neighbouring atoms within a distance \( r_c \) of a particular atom, a technique that was first suggested by Verlet [56]. In his method a skin is added to the cutoff radius \( r_c \), large enough such that no atom can travel through it in one time step, resulting in a larger sphere of radius \( r_l \). Initially a neighbour list is constructed for each atom in the system using this larger radius, \( r_l \). The neighbour list need only be updated when the sum of the magnitudes
Spatial decomposition

When dealing with larger systems ($\gtrsim 1,000$ atoms) it becomes advantageous to decompose the simulation cell into smaller regions (or boxes). This is known as spatial decomposition. A rectangular simulation cell of dimensions $L_x \times L_y \times L_z$ is split into a mesh of $N_x \times N_y \times N_z$ boxes in the $x$, $y$ and $z$ directions respectively. The number of cells in the $x$ direction is chosen such that $N_x$ is the largest integer $\leq L_x/r_l$ [2], where $r_l$ is the neighbour list cutoff size. $N_y$ and $N_z$ are chosen in the same manner. The $x$ index of the box containing an atom with position $(r_x, r_y, r_z)$ is calculated in the following way:

$$C_x = \text{(int)} \frac{(r_x - X_{\text{min}})}{W_x},$$

(2.30)

where $W_x$ is the width and $X_{\text{min}}$ the minimum position of the boxes in the $x$ direction, and “int” means to take the integer value. The $y$ and $z$ indices, $C_y$ and $C_z$, are calculated in
Table 2.8: The complexities of computation and communication, and the memory requirements, associated with different parallelisation strategies. $N$ is the number of atoms in the system and $P$ is the number of processors. Taken from [64].

<table>
<thead>
<tr>
<th>Method</th>
<th>Computation</th>
<th>Communication</th>
<th>Memory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replicated data</td>
<td>$O(N/P)$</td>
<td>$O(N)$</td>
<td>$O(N)$</td>
</tr>
<tr>
<td>Data partitioning</td>
<td>$O(N/P)$</td>
<td>$O(N/P)$</td>
<td>$O(N/P)$</td>
</tr>
<tr>
<td>Spatial decomposition</td>
<td>$O(N/P)$</td>
<td>$O((N/P)^{2/3})$</td>
<td>$O(N/P)$</td>
</tr>
</tbody>
</table>

the same manner. The box index of the atom can then be calculated using the following formula:

$$boxIndex = \text{(int)} \left( C_x + C_z N_x + C_y N_x N_z \right).$$

(2.31)

With the boxes constructed in such a way it is possible to use an improved neighbour list technique: the linked cell method. Since the sides of the boxes are at least the size of the cutoff and skin, $r_t$, then neighbouring atoms must either be within the same box, or one of the neighbouring 26 boxes, of the concerned atom. Figure 2.2 shows a 2-dimensional illustration of this, with neighbouring atoms to the red atom found only in the same box and the surrounding eight boxes. Thus when constructing the neighbour list you only need search over these boxes for neighbouring atoms. The efficient linked list method of storing neighbouring atoms is used with this method [54] and reduces the force calculation from $O(N^2)$ to $O(N)$.

**Parallelisation**

Another essential performance optimisation is the use of parallel computing, especially when dealing with larger system sizes. A number of differing strategies exist for achieving this (see [64]), perhaps the most basic being the “replicated data” technique. Here each processor stores a copy of the entire set of atoms but only works on the atoms assigned to it. This method has a large overhead in communication since any change to the data associated with a single processor has to be communicated to every other processor. The memory requirements of this strategy are also high. A better approach is the “data partitioning”
technique in which only the atoms required to carry out the force computation are stored on the processor. Related to this approach is the “spatial decomposition” method. In this method the simulation cell is decomposed between processors in the way discussed in the previous section, i.e. each processor works only on the atoms within its domain. The communication overhead of this method is low since the processor already “owns” most of the particles it requires. It only needs to obtain information about the atoms close to its boundary in adjacent cells, i.e. those atoms within range of the neighbour list cut-off. Table 2.8 summarises the efficiency of these approaches. The LBOMD programme uses the method of spatial decomposition as its parallelisation strategy.

2.1.6 Computing electrostatics

Due to the long range nature of the Coulomb potential (Equation 2.17) it must be evaluated separately to the other, shorter range, potentials. Specifically we cannot make use of the neighbour lists mentioned earlier since we must take account of the interaction of a particular atom with all other atoms in the system, a computation of the order $\mathcal{O}(N^2)$. Calculations of this order must be avoided when dealing with large systems since they scale badly. In aid of this a number of methods have been developed that approximate the $\mathcal{O}(N^2)$ computation with one of a lower order.

**Ewald method**

For periodic systems you could use a method such as the Ewald sum [78] which works by decomposing the electrostatic potential into short and long range components. The short range component sums quickly in real space while the long range component sums quickly in Fourier space. However computation of the Ewald method takes $\mathcal{O}(N^{3/2})$ calculations. More recent developments, such as the smooth particle mesh Ewald method [79], improve the speed of the algorithm to $\mathcal{O}(N \log N)$. 
Distributed Parallel Multipole Tree Algorithm

Another technique is the Distributed Parallel Multipole Tree Algorithm (DPTMA) [80], that can be applied to systems using non-periodic boundaries. This method is part of a class of algorithms known as Fast Multipole Algorithms (FMA), developed originally by Greengard and Rokhlin [81]. These methods work on the idea that a group of charged particles a long distance from another charged particle will appear as a single point charge to that particle. The simulation region is decomposed into cells using a tree algorithm, such as the one by Barnes and Hut [82], and the charge of a well separated cell is described by a multipole expansion at the centre of the cell [83]. The computational complexity of these algorithms is $O(N \log N)$, or even $O(N)$ in some situations. The DPMTA is an efficient implementation of this method that has been parallelised using MPI, allowing for large electrostatic systems to be simulated. This was the algorithm used to compute electrostatic forces for most of the work done in this thesis.

CUDA All-Pairs method

The advent of general purpose computing on graphics processing units (GPGPU) in recent years has been an interesting development in the field of scientific programming. At the forefront of this technology is NVIDIA’s parallel computing architecture CUDA (Compute Unified Device Architecture). Programming on graphics processing units (GPUs) is advantageous when dealing with massively parallel problems, of which the molecular dynamics force calculation is one. Rather than executing one thread quickly as a CPU does, the GPU is designed to execute many concurrent threads simultaneously, albeit at a slower clock speed. Since access was available to a CUDA capable GPU a simple “all-pairs” method was written for comparison with the the highly optimised DPMTA library on a CPU. The “all-pairs” method was adapted from the one found in [84] for calculating the gravitational potential of a N-body system, to calculate the Coulomb potential. It is a brute force approach, taking $O(N^2)$ computations, and would not be feasible when running on a CPU for anything other
The method works by considering the $N^2$ computations required for the force calculation as a $N \times N$ grid, as shown in Figure 2.3. A square on the grid in row $i$ and column $j$ represents the contribution to the force acting on atom $i$ by atom $j$. Thus to calculate the total force, $F_i$, acting on atom $i$ we sum all the contributions in row $i$ of the grid. The $N$ rows of the grid are broken up into $N/p$ blocks, each containing $p$ rows (or threads). GPUs consist of multiprocessors which themselves contain 8 processors. A multiprocessor is capable of executing a large number of threads in parallel, each of which has access to fast, local shared memory. With the grid broken down in this way each block is sent to run on a multiprocessor. Each thread in the block sums the forces for one atom in the system, i.e. sums the interactions along one row of the grid. To make use of the shared memory available to each multiprocessor on the GPU a “tile” system is used. Each of the $p$ threads in a block read one atom’s data (corresponding to a column in the grid) into shared memory, after which the threads are synchronised. This $p \times p$ square is the “tile”. Then the threads calculate the forces contributed to their atom by the atoms in shared memory. The
threads are synchronised again, the next \( p \) atoms (columns) are read into shared memory, and the process continues. A number of blocks execute in parallel depending on how many multiprocessors the GPU contains (the card we used contained 30 multiprocessors). The number of threads in a block is limited to 512 with the GPU that was used in this work, although in practice we took \( p = 256 \) threads per block. Thus \( 30 \times 256 = 7,680 \) threads are executed in parallel. Blocks that are not running are queued until a multiprocessor is available for them to run on.

The CUDA all-pairs method was applied to systems of up to 150,000 atoms and was found to perform better than the serial DPMTA method for similar levels of accuracy. The difference in speed between the two methods depended on the parameters used with the DPMTA method, i.e. the number of terms in the multipole expansion and the levels of spatial decomposition. The more terms and fewer levels used, the smaller the error in the DPMTA force calculation, but the longer it takes. The all-pairs method is an exact calculation. A simple test was carried out on HfO\(_2\) systems of varying sizes from 12,000 to 146,004 atoms. The DPMTA method was performed on one processor of an 8 core 2.26 GHz Intel Mac Pro. The CUDA method was carried out on a NVIDIA GTX 285 graphics card on the same
machine. The same DPMTA parameters were used throughout and were chosen to give the best performance and accuracy over the range of systems (5 levels of spatial decomposition and 5 terms in the multipole expansion). Figure 2.4 shows the times taken for each method to calculate the electrostatics for the different system sizes. The CUDA method clearly performs better than the serial DPMTA method over the entire range. In practice, as the system size increases you would begin to use parallel processing on the CPU to improve performance. For example, on 4 processors the DPMTA electrostatics calculation on the largest system would take 5.8 s, instead of 17.3 s on 1 processor (still slower than the CUDA method). However the advantage of calculating neighbour lists in parallel would offset this deficit in performance of the force calculation. Ideally we would integrate the CUDA all-pairs method with the parallel version of LBOMD, and also use CUDA to accelerate other parts of the code, but this was outside the scope of this thesis.

2.1.7 Boundary conditions

Choice of boundary conditions is essential to performing a realistic simulation and depends on the type of simulation you are carrying out.

Fixed boundaries

One technique is to use fixed boundaries where the outside few layers of the system are held fixed. It is important when using this method that the simulation cell is large enough that any cascades are not influenced by boundary effects. This method would typically be used when modelling ionic systems using the multipole method, or for modelling high energy cascades as it allows the use of a thermal layer (discussed later) to dissipate excess energy from the system. This has the effect of making the simulation cell appear as if it were part of a much larger cell. Generally when performing ion bombardment simulations with impacts occurring across the top surface, at least the bottom surface would be held fixed to ensure that momentum transfer does not cause the entire cell to move.
Periodic boundaries

An alternative to fixed boundaries is the periodic boundary condition (PBC). In this case the simulation cell is replicated in each direction forming an infinite lattice. An atom leaving the cell through one face re-enters the cell via the opposite face. When simulating energetic cascades it is important to ensure the simulation cell is large enough that the cascade does not interact with its periodic images. PBCs must also be taken account of when analysing a simulation, for example the minimum image convention should be applied when calculating the separation between two atoms [54]. Immediately after calculating the $x$ separation of two atoms, $r_{ij}^x$, you would apply the following statement:

$$r_{ij}^x = r_{ij}^x - L_x \times \text{round}(r_{ij}^x / L_x),$$

(2.32)

where $L_x$ is the length of simulation cell in the $x$ direction, and “round” is a function that returns the nearest integer to a given number. Such a calculation is performed in each direction in which PBCs are being applied.

Thermal boundary layers

An additional boundary condition that warrants mention is the thermal boundary layer. This is usually applied to a specified number of layers of atoms within a fixed boundary layer, and is used to regulate the temperature of the simulation cell. This type of boundary condition is usually applied when simulating high energy cascades or multiple impacts, to remove excess energy introduced into the system and to maintain it at the desired temperature. Ideally, if you could simulate a large enough system, the energy from these impacts would dissipate throughout the system. However since we can only simulate small systems the temperature would increase rapidly. The effect of being part of a much larger simulation is simulated by damping or increasing the velocities on the atoms within the thermal layer.

The Berendsen et al thermostat [85] maintains the temperature of the system by cou-
pling it to an external heat bath. The velocities are scaled such that the rate of change of temperature is proportional to the difference in temperature between the bath and the system:

\[
\frac{dT(t)}{dt} = \frac{1}{\tau}(T_0 - T(t)),
\]

where \(T(t)\) is the temperature of the system at time \(t\) and \(\tau\) is a coupling parameter determining how tightly the bath and system are coupled together. With this method the system temperature converges exponentially to the desired temperature. Other methods include Langevin dynamics and the Nosé-Hoover algorithm [86, 87]. In this work the Berendsen thermostat is used due to the speed at which the desired temperature is reached.

2.1.8 System equilibration

At the beginning of a simulation it is necessary to ensure that the atoms in the lattice are in their minimum energy configuration. While you can create the lattice with the experimental lattice parameters this will not always represent the minimum energy configuration, especially when dealing with long range potentials (electrostatics). It is also sometimes necessary to relax a system at different stages of a simulation, for example after each impact of a multi impact simulation, to avoid cumulative increases in energy. Equilibration, or relaxation, techniques are used to achieve this.

One method that is employed in the LBOMD programme is the method of conjugate gradients [88]. This was the technique that tended to be used when the lattice configuration was already close to a minimum energy configuration, i.e. prior to the start of the simulation.

Another method implemented in the LBOMD programme is the damped MD technique. In this method the system of atoms oscillate on the potential energy surface. These oscillations are systematically damped until the system comes to rest at a minimum. This method was used when the system was not close to equilibrium, for example between multiple ion impacts.
2.2 Multi time scale dynamics

2.2.1 Introduction

While MD is an extremely powerful method for investigating many processes on an atomic level, one of the major drawbacks it has is the time scales that can be achieved during simulations. Time steps in MD simulations tend to be of the order of $1 \times 10^{-15}$ s, thus simulations are generally limited to the order of nanoseconds to microseconds. For some processes, such as sputtering induced by a single ion bombardment, this does not pose a problem since these processes are known to occur on very small timescales (picoseconds). However diffusion processes occurring between ion impacts occur on a much longer time scale and are therefore out of reach of MD simulations.

In order to overcome this problem of differing time scales we use a multi time scale dynamics (MTSD) method: MD is used to model the ballistic phase, i.e. the ion bombardment, and then we use a Monte Carlo technique [89] to model the slower processes. Kinetic Monte Carlo (KMC) utilises harmonic transition state theory approximations [90] to simulate the time evolution of a system without biasing its dynamics. As an input KMC requires a list of all possible transitions the system can undergo along with the associated energies. From these energies the rates at which the transitions occur can be calculated using the Arrhenius equation:

$$k_i = A_i \exp\left(-\frac{E_i}{k_B T}\right),$$

(2.34)

where $k_i$ is the rate, $A_i$ the prefactor, and $E_i$ the energy barrier of the $i$'th transition. $T$ is the temperature of the system and $k_B$ the Boltzmann constant. The prefactor, $A_i$, can be calculated using Vineyard’s method [91]. However since this is an expensive calculation and the transition rate depends much more strongly on $E_i$ than $A_i$, which was found to vary by only a small amount, the prefactor was set to a fixed value $A_i = \nu$ for all $i$. A good value for the prefactor was found to be $\nu = 10^{13}$ s$^{-1}$ [92, 93].

Once the rates are determined an event is chosen by selecting a random number between
0 and $P_T = \sum_i k_i$, and performing another sum over $k_i$ until the chosen random number is exceeded. The transition associated with the last rate before the random number was exceeded is selected. The time associated with the selected transition is given by:

\[ t_s = -\frac{\log u}{\sum_i k_i}, \]  

where $u$ is a random number between 0 and 1 representing the stochastic nature of the simulation.

Pre-definition of all possible events, while achievable when dealing with simple and symmetric crystal structures, becomes a problem when dealing with more complex or defective systems. Henkelman and Jónsson attempted to overcome this problem with their on-the-fly kinetic Monte Carlo (otfKMC) method [94]. In this scheme they calculate transitions on-the-fly at the beginning of each step. This is achieved by using a saddle point finding algorithm followed by another algorithm that accurately determines the height of the discovered barrier. Both these techniques generally work using the concept of representing $N$ points in 3-dimensional space as a single point on a $3N$-dimensional potential energy surface.

The MTSD programme used in this work was originally written by Louis Vernon at Loughborough University for his thesis [93], where he goes into a detailed explanation of the algorithm. The programme was written in Perl and interfaces with the LBOMD MD programme whenever a force evaluation is required. The MTSD algorithm is summarised in Figure 2.5 and combines MD with otfKMC. Initially an ion impact, called an external event, is carried out using MD. Following this the transition searches are started and the system is advanced step by step. At each step there is the possibility of a further external event occurring, or one of the discovered transitions. In order to optimise performance, transition searches are performed only on areas of the lattice that are defective. All the defects in the system are identified and included in the subsystem along with atoms in the vicinity of the defective atoms. This subsystem is then used for the transition searches. This method is
First step?
Identify defects
Run transition searches / external events
Found saddle point?
Calculate barrier
Search limit exceeded?
Calculate rates of transitions and external events
Select event
Run external events
Start

Figure 2.5: The on-the-fly kinetic Monte Carlo multi time scale algorithm.
2.2. MULTI TIME SCALE DYNAMICS

Figure 2.6: Image showing one step of the RAT method. First the point $R'_i$ is offset to give $R_{i+1}$. Then the perpendicular force, $F_P$, acting on this point with respect to the offset vector is minimised to give the new point, $R'_{i+1}$

much less time consuming than if you were to include the entire system in the searches.

2.2.2 Saddle point finding methods

As mentioned earlier, saddle point finding methods are used in the otfKMC scheme to find possible transitions. The main feature of these methods is that they require only the initial configuration of the system in order to return local saddle points. All these techniques work in a similar way by locating and following the lowest curvature mode, along which the saddle point is a maximum. Early methods involved calculating the Hessian matrix \[95, 96\] but these scale poorly with system size. More recent methods, such as the activation-relaxation technique (ART) of Barkema and Mousseau \[97\] and the dimer method developed by Henkelman and Jónsson \[98\], work by estimating the lowest curvature mode at a point without evaluating the Hessian.

Relaxation and translation method

The saddle point finding method used in this work is the relaxation and translation (RAT) technique developed by Louis Vernon \[93\]. This method works by offsetting a point and then minimising the perpendicular force acting on the new point with respect to the displacement from the previous point (see Figure 2.6). To get from one configuration, $R'_i$, to the next,
where \( N_{i+1} \) is the displacement vector that will be discussed later. The forces acting on point \( R_{i+1} \) are decomposed into parallel and perpendicular (\( F_P \)) components with respect to the displacement vector \( N_{i+1} \). The new point, \( R'_{i+1} \), is then obtained by minimising \( F_P \) and a new vector is created linking the new position to the previous one:

\[
N'_{i+1} = R'_{i+1} - R'_i. \tag{2.37}
\]

We now define the displacement vector, \( N_{i+1} \), as:

\[
N_{i+1} = \frac{N_i + N'_i}{||N_i + N'_i||}. \tag{2.38}
\]

The initial displacement vector, \( N_1 \), is populated with random numbers between \(-1\) and \(1\) and normalised. The saddle point was detected by taking the dot product of the displacement between the current position and the initial position with the force acting on the current position. When this is positive you have crossed the saddle point.

### 2.2.3 Barrier calculation methods

Once a transition has been identified we need a method to accurately calculate the height of the barrier (the saddle point) associated with the transition. Although the methods mentioned in the previous section will find saddle points, they only provide a loose estimate of the actual energy barrier associated with the saddle. In fact, due to the way they work (searching up hill from a minimum) they will often overestimate the saddle point. Thus a different set of techniques are required to accurately determine the energy barrier associated with a transition. These techniques require both the initial and final configurations of the
transition. Examples of such methods are the string method [99] and its many variations [100, 101].

Nudged Elastic Band method

One of the most popular techniques for calculating transition barrier energies, and the one used in this work, is the nudged elastic band (NEB) method of Jónsson et al [102], improved by Henkelman et al with the climbing image NEB method [103]. The NEB method returns the height of the energy barrier associated with the given initial and final minimum energy configurations of the transition, along with the minimum energy pathway (MEP) between these points.

The NEB is initialised by linearly interpolating between the initial and final configurations of the system, creating a band of $m$ evenly spaced images, $R_0, \ldots, R_m$. Spring forces are introduced between images to ensure their spacing remains even. In order to avoid interference between the spring force and the true force, these forces are decomposed into parallel and perpendicular components with respect to the tangent at that point. This is shown in Figure 2.7. The unit tangent vector is estimated in the following way (and then normalised)
\\[ 40 \text{ CHAPTER 2. METHODOLOGY} \]

where \( V_i \) is the potential energy of image \( i \), and \( V_i^{MIN} \) and \( V_i^{MAX} \) are the maximum and minimum of \( |V_{i+1} - V_i| \) and \( |V_i - V_{i-1}| \) respectively. The NEB method defines the force acting on image \( i \) as:

\[
F_i = F_i^S + F_i^P,
\]  

(2.40)

where \( F_i^P \) is the projection of the true force acting on image \( i \) perpendicular to the tangent vector, and \( F_i^S \) is the spring force parallel to the tangent vector \( \hat{\tau}_i \), given by:

\[
F_i^S = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|)\hat{\tau}_i,
\]  

(2.41)

where \( k \) is a spring constant. Once all the forces have been calculated the images are relaxed simultaneously by translating the \( m \) points in \( 3N \) space to one point in \( 3Nm \) space. In this way the band moves iteratively towards the MEP.

One problem with the original implementation of the NEB is that often the maximum point on the MEP (the saddle) will occur between two images, resulting in an inaccurate transition barrier energy. The climbing NEB method [103] resolves this issue by allowing the image with the highest energy to move along the MEP to the highest point. This is achieved by modifying the force, \( F_{i_{max}} \), acting on the highest energy image after several minimisation iterations, in the following way:

\[
F_{i_{max}} = F_i - 2F_i^||,
\]  

(2.42)

where \( F_i^|| \) is the component of the true force parallel to the tangent vector \( \hat{\tau}_i \), and the spring
force is ignored. Using this technique the climbing NEB method finds the maximum along the MEP (the saddle point).

2.2.4 Parallelisation

The parallelisation of the MTSD code was improved during the course of this thesis. At the start of each step $P - 1$ processes, where $P$ is the number of available processors, were forked to perform transition searches (i.e. the RAT method followed by the NEB method). The final processor was used to carry out the “external event” (the ion impact). Then the rates of the transitions and the external event were calculated and one was chosen, as discussed previously. The searches were terminated when the deposition had finished and the specified minimum number of attempted searches was exceeded. If the deposition finished before the minimum number of searches condition was met then that process started doing transition searches too. Inter-process communication between the forked processes was achieved using the perl IPC-Shareable module [105] and a shared memory variable. The forked processes were terminated at the end of each step using the Proc-ProcessTable perl module [106], which gave access to the system process table. The code was also adapted so that it would run on Loughborough University’s high performance computer, hydra (a 1,956 core 64-bit Intel Xeon cluster supplied by Bull).

2.3 Analysis techniques

2.3.1 General

Generally the work in this thesis was split into two sections: running the simulations and analysing them. The techniques used to run the simulations have already been discussed. To analyse the results of the simulations custom scripts and programmes were written in a combination of Python and C. Python was chosen due to the speed of programming and ease of use, as well as the vast array of external libraries that exist to enhance it [107], for
example: Matplotlib for plotting graphs [108], and NumPy and SciPy for scientific routines
and arrays [109]. Python by itself would be too slow when dealing with very large systems
and computationally expensive calculations, so C libraries were written to perform these
tasks and were linked to the Python scripts using SWIG (Simplified Wrapper and Interface
Generator) [110]. Interactive visualisation of the simulations was made possible using AVAS
(Atomistic Visualisation and Analysis Software), originally written by Marc Robinson and
documented in his thesis [111]. This programme was modified for use in this thesis, for
example by adding the ability to analyse the MTSD simulations and adapting it for use
under Mac OS X 10.6 Snow Leopard. Many of the images in this thesis were produced using
the Persistence of Vision Raytracer (POV-Ray) [112], capable of producing very high quality
images even when visualising millions of atoms.

2.3.2 Cluster analysis

Cluster detection

The first step in identifying clusters of atoms ejected from a lattice is to obtain a list of all
the atoms that have been ejected. In this thesis the top surface (in the \(y\) direction) of the
lattice was taken as the free surface, while the other boundaries were either fixed or periodic.
All atoms outside fixed boundaries are assumed to have been ejected from the lattice and
are automatically added to the search list. All remaining atoms are put into bins by their
\(y\) position. When searching up from the bottom bin, the first bin containing no atoms is
assumed to be the top of the lattice and all atoms above this are also added to the search
list.

The region containing atoms in the search list is spatially decomposed to greatly improve
the speed of the algorithm – instead of searching the full list of atoms for a neighbouring
atom you search only those in the surrounding cells. A simple recursive algorithm is used
to find all atoms belonging to a cluster. The only parameter needing to be specified is the
maximum separation between two atoms for them to still be considered neighbours (typically
2.3. ANALYSIS TECHNIQUES

chosen to be 3.5 Å). This algorithm is shown in Figure 2.8.

**Temperature calculation**

In order to calculate the temperature of a cluster of atoms the kinetic energy of the cluster must be broken down to obtain the internal vibrational energy, from which the temperature is calculated [113]. The centre of mass of the cluster, \( \mathbf{R} \), is given by the following equation:

\[
\mathbf{R} = \frac{1}{M} \sum_i m_i \mathbf{R}_i,
\]  

(2.43)

where \( M = \sum_i m_i \) is the total mass of all atoms in the cluster, and \( \mathbf{R}_i \) is the position vector of the \( i \)'th particle from the origin. The velocity of the centre of mass, \( \mathbf{V} \), is given by:

\[
\mathbf{V} = \frac{1}{M} \sum_i m_i \mathbf{V}_i,
\]  

(2.44)
where $V_i$ is the velocity of atom $i$. The kinetic energy of the centre of mass is:

$$T_{COM} = \frac{1}{2}M||V||^2. \quad (2.45)$$

Now we define $r_i = R_i - R$ as the displacement of atom $i$ from the centre of mass, and $v_i = V_i - V$ as the velocity of atom $i$ relative to the centre of mass. The angular kinetic energy of the cluster is given by the following equation:

$$T_{ANG} = \frac{1}{2} \sum_i \omega_i \cdot L_i, \quad (2.46)$$

where the angular momentum, $L_i$, of atom $i$ is given by:

$$L_i = m_i (r_i \times v_i), \quad (2.47)$$

and the angular velocity, $\omega_i$, of atom $i$ is given by:

$$\omega_i = \frac{r_i \times v_i}{||r_i||^2}. \quad (2.48)$$

Thus Equation 2.46 can be rewritten as follows:

$$T_{ANG} = \frac{1}{2} \sum_i m_i \frac{||r_i \times v_i||^2}{||r_i||^2}. \quad (2.49)$$

The internal vibrational energy of the cluster, $T_{INT}$, is given by the following formula:

$$T_{INT} = T_{TOT} - T_{COM} - T_{ANG}, \quad (2.50)$$

where $T_{TOT}$ is the total kinetic energy of the cluster. The temperature of the cluster, $C_T$, is then calculated as follows:

$$C_T = \frac{2T_{INT}}{3k_BN}, \quad (2.51)$$
where $k_B$ is the Boltzmann constant and $N$ is the number of atoms in the cluster.

**Summary**

The cluster detection and temperature analysis will mainly be used in Chapter 4 for analysing the debris in the wake of a bullet impact on armour plating.

### 2.3.3 Surface analysis

The technique used to detect the height of the surface of a lattice was to split the lattice into columns and then split the columns into cells. Then iterate up through the cells in a column until you find two empty cells in a row. The height of the highest atom in the last cell that contained atoms is then taken as the height of the surface in that column. This is done for all columns and an average value is obtained. To measure the roughness of the surface we calculate the root mean square (RMS) of the deviation of the height of each column from the average surface height, using the following formula:

$$R_{RMS} = \sqrt{\frac{1}{N_c} \sum_{i=1}^{N_c} s_i^2},$$

(2.52)

where $s_i$ is the difference in height of column $i$ from the average column height, and $N_c$ is the number of columns.

The surface height and roughness analysis methods will be utilised in the Chapters 5 and 6, where surface erosion is modelled using different techniques.

### 2.3.4 Point defects

One way to quantify damage in a crystal lattice is to look for point defects, of which three types will be considered here. A vacancy is simply a lattice site that should contain an atom but does not, while an interstitial is an atom that does not occupy a normal lattice site.
Finally an antisite is a site that contains an atom of a different specie to the one that should be on it.

In order to find defects we require two configurations of the system: the initial, reference configuration and the input lattice. First we identify all atoms in the input lattice that have moved from their original positions by more than a specified distance, the vacancy radius, typically 1 to 1.3 Å. This leaves us with a list of possible vacancies (i.e. the reference positions of atoms that have moved) and a list of possible interstitials (their positions in the input lattice). Next we spatially decompose the possible vacancies into cells with sides at least the size of the vacancy radius. We then iterate over the possible interstitials and find which cell they belong to, along with the neighbouring 26 cells (as discussed in the spatial decomposition section). By comparing the position of the possible interstitial with the positions of the possible vacancies in the neighbouring cells, we can classify it in the following way:

- The possible interstitial occupies a possible vacancy site of the same specie ⇒ the atom has exchanged positions and is not a vacancy
- The possible interstitial occupies a possible vacancy site of a different specie ⇒ we have found an antisite
- The possible interstitial does not occupy a possible vacancy site ⇒ it is an interstitial.

By updating the list of possible vacancies when they are filled we can obtain a list of actual
vacancies. In a closed system, i.e. one with no free surfaces, the number of interstitials and vacancies (known as Frenkel pairs) should be the same. When performing surface impacts the number of vacancies will equal the sum of the number of interstitials, adatoms and sputtered atoms, minus the number of incoming ions. Defects are visualised in the manner shown in Figure 2.9.

The point defects analysis technique will be used throughout all the results chapters as a way of quantifying damage in the systems that are being modelled. In addition to this, a simpler method of detecting displaced atoms (atoms that have moved from their initial positions) will also be used.
Chapter 3

Swift heavy ion bombardment

3.1 Introduction

Swift heavy ion irradiation has been a topic of discussion for many years [27]. These ions are characterised by their very high energies, typically in the MeV (or greater) range. A large amount of experimental work has been performed on this topic [19, 114, 115, 116, 117] and many interesting features have been observed in the wake of the ions. Due to the large amounts of energy involved these features are formed due to the electronic stopping force of the ions in the material. Such features include interesting surface topographies – for example in the papers by Garrido et al [19] and Skuratov et al [116] we see the formation of large hillocks on the surfaces of the irradiated materials. Experimental work on sputtering following swift heavy ion irradiation has also been investigated [117]. In addition to these interesting surface features, the passage of the swift heavy ion in the material can create a heavily damaged, cylindrical region around the trajectory of the ion, known as a ‘latent track’ or ‘ion track’ [115].

Many computational studies have also been carried out on swift heavy ion bombardment to understand the mechanism behind the formation of ion tracks or other effects, for example sputtering due to the impact of the ion. The work by Bringa et al [43] simulates electronic
sputtering using MD, while Pakarinen et al [44] investigate the formation of ion tracks using MD and a thermal spike model.

A number of models have been proposed for modelling swift heavy ions passing through a material. A thermal spike model [28, 42] describes the transport of energy out of a heated region (the track). The thermal spike is a region of high temperature around the trajectory of the heavy ion. If the temperature is high enough this can result in the formation of an amorphous phase – the ion track. The initial distribution of energy within the thermal spike region is here modelled using a Gaussian distribution [28], but could also be described by the profiles determined in the work by Waligorsky et al [118].

In this chapter classical molecular dynamics (MD) simulations were carried out to investigate the development of surface topographies following irradiation by swift heavy ions. Two models for the swift heavy ion passing through the material are implemented using MD: a thermal spike and a charge stripping model. Some results obtained from the work done in this chapter have been published in the following papers: [119, 120].

3.2 HfO$_2$–MgO interface system

3.2.1 Background

Dispersion fuel forms are a key area of interest in advancing nuclear technology. This type of fuel is a mixture of a fissile material dispersed within a non-fissile host matrix, where the properties of the host matrix should facilitate separation of the fission products into a reusable form. A potential dispersion fuel is the UO$_2$–MgO composite material.

Experimental studies, such as the one by Valdez et al [122], have been conducted on the HfO$_2$–MgO interface, where HfO$_2$ is used as a surrogate for the fissile core (UO$_2$) for experimental convenience. They have shown this interface to have very good radiation tolerance. In addition it has long been known that hafnia (and hafnia based materials) will be important to the nuclear industry due to their exceptionally high neutron absorption
Another experimental study by Usov et al [121] has also studied this interface. The authors present results obtained by irradiating a tri-layer HfO$_2$–MgO–HfO$_2$ structure with 10 MeV gold ions. Figure 3.1 shows an interesting result they found: they saw craters forming in the HfO$_2$ surface with raised central regions (“spires”). The craters were very large, approximately 10 microns in diameter at the surface and the “spires” found within the craters are roughly 100 nm tall. The mechanism behind the creation of these “spires” is unknown. We have carried out computer simulations of swift heavy ion bombardment of this interface in an attempt to understand the mechanism behind the formation of these features.

### 3.2.2 Constructing the interface

The interface between the HfO$_2$ and MgO layers was constructed as described by Echigoya for the ZrO$_2$–MgO interface in a solidified eutectic [124]. This involved fitting the HfO$_2$ \{0 1 0\} surface to the MgO \{1 1 1\} surface and results in there being layers of metal, oxygen, metal, oxygen (and so on) throughout the material (see Figure 3.2). This method creates
a stable interface and has previously been used successfully in computer simulations [125], where density functional theory analysis was used to study fission product incorporation in alkaline earth metal oxides, such as MgO.

The system consisted of a bilayer of MgO and HfO$_2$, with a free surface of either species, as shown in Figure 3.3. The free surface will normally consist of HfO$_2$ since this was the surface the ions were hitting in the experiments. However we also conducted simulations across a MgO free surface.

Figure 3.4 shows the MgO $\{1\ 1\ 1\}$ surface which contains only Mg atoms. If we were to make this surface free then it would explode – we are using a fixed charge potential and so the surface would be highly polarised. In order to stabilise the surface we remove half of the Mg atoms from this surface. This leaves us with another problem: since the number of Hf atoms on the opposite surface does not match the number of Mg atoms on the free surface (the lattice constants do not match), the system is not charge neutral. Thus we
adjust (slightly) the charges on the opposite (fixed) Hf surface to ensure the system has a net charge of zero. In the case of selecting the HfO$_2$ surface to be free we have the same problem and solve it in the same way. Different alignments are tested for minimum energy and, once relaxed, this method creates a stable surface through which particle impacts may be simulated. In both the case of the HfO$_2$ free surface and the MgO free surface we see some surface reconstruction during simulations, as a result of the removal of atoms from the surface. The surface reconstruction will be shown in figures later in the chapter.

3.3 Methodology

3.3.1 Computational method

The interatomic potentials used during this chapter have been described in detail in the methodology chapter (Section 2.1.4). Buckingham, Lennard-Jones and repulsive ZBL potentials are all used. Electrostatics were calculated using the DPMTA library or the CUDA all-pairs method for smaller systems. Figure 3.3 shows a diagram of the system (in the case of a single material system ignore the interface line). Here the top surface is free: this is the surface ions are fired across. Atoms around the edges of the simulation box were held fixed. The charges of fixed atoms were adjusted so that the boundaries were not polarised.
Table 3.1: The different systems that were used in the ion bombardment simulations. Surface area is the area of the free surface (the free surface is square). If there is more than one material in the system: the interface depth is measured from the free surface and the free surface consists of the material listed first.

<table>
<thead>
<tr>
<th></th>
<th>Number of atoms</th>
<th>Material</th>
<th>Surface area (nm$^2$)</th>
<th>System depth (nm)</th>
<th>Interface depth (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>349,648</td>
<td>MgO</td>
<td>17.0 × 17.0</td>
<td>10.7</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>761,788</td>
<td>MgO</td>
<td>17.8 × 17.8</td>
<td>21.4</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>79,446</td>
<td>MgO–HfO$ _2$</td>
<td>9.3 × 9.3</td>
<td>9.2</td>
<td>4.6</td>
</tr>
<tr>
<td>D</td>
<td>152,182</td>
<td>MgO–HfO$ _2$</td>
<td>12.9 × 12.9</td>
<td>9.2</td>
<td>4.6</td>
</tr>
<tr>
<td>E</td>
<td>250,274</td>
<td>HfO$ _2$–MgO</td>
<td>16.5 × 16.5</td>
<td>10.6</td>
<td>4.6</td>
</tr>
<tr>
<td>F</td>
<td>299,487</td>
<td>HfO$ _2$–MgO</td>
<td>16.5 × 16.5</td>
<td>10.6</td>
<td>3.1</td>
</tr>
<tr>
<td>G</td>
<td>725,034</td>
<td>HfO$ _2$–MgO</td>
<td>25.8 × 25.8</td>
<td>10.6</td>
<td>3.1</td>
</tr>
</tbody>
</table>

and the system had a net charge of zero [71]. The simulations were always started from 0 K. A thermostat was used in all charge stripping and thermal spike model simulations, to remove excess energy from the system. The thermostat we utilised was the Berendsen et al thermostat [85], with time constant $\tau = 1$ ps (see Equation 2.33). The thermostat was applied to atoms within 2 nm of the fixed boundaries. Details of the different systems are shown in Table 3.1.

### 3.3.2 Single particle and cluster bombardment

Single particle bombardment of systems with either a HfO$_2$ or MgO free surface were performed. Impacts were always normal to the surface. In the case of multiple sequential impacts an impact is performed for a specified amount of time, typically 20 ps, after which a damped MD stage is carried out for typically 5 ps. This ensures there is no excess energy in the system when the next impact is simulated.

### 3.3.3 Thermal spike model

Our thermal spike model involves the deposition of kinetic energy into a cylindrical region around the path of the swift heavy ion, as shown in Figure 3.5. We have assumed that the radial distribution of kinetic energy in this region can be approximated by a Gaussian
3.3. METHODOLOGY

Figure 3.5: The initial thermal spike cylinder at the centre of the lattice, centred around the path of the swift heavy ion. All other atoms start with zero kinetic energy.

Figure 3.6: The initial distribution of kinetic energy (temperature) within the thermal spike for an electronic energy loss of 6.8 keV/nm. The radius of the spike is 2 nm. The radial distribution of energy in this region is determined from a Gaussian distribution.
distribution. Similar assumptions have been made by other authors [28, 126]. The radial distribution of energy around the path of a heavy ion has been investigated by many other authors, including Waligorski et al [118], who consider a decrease in the energy as the inverse of the square of the radial distance from the ions path.

The atoms within the cylindrical thermal spike region in our model are given random directions, and all atoms outside the spike region start the simulation with zero kinetic energy. A spike diameter of 4 nm, noted as a typical value in [19], was chosen for the thermal spike cylinder. The Gaussian function:

\[
f(x) = a \exp\left(-\frac{x^2}{2c^2}\right),
\]

was constructed by choosing a peak temperature at the centre of the spike region, \( h \), and a tolerance, \( v \), such that at the edge of the thermal spike region, where \( x = d \), we have \( v = h \exp(-d^2/2c^2) \). Solving for the variance, \( c^2 \), gives:

\[
c^2 = -\frac{d^2}{2 \ln(v/h)}.
\]

The peak temperature, \( h \), is chosen to give the desired electronic energy loss for the given spike radius, \( d \). Figure 3.6 shows the initial distribution of kinetic energy in the thermal spike for our model for \( d = 2 \) nm and \( h = 561,000 \) K. In this particular example (taken from Section 3.5.3) this resulted in an electronic energy loss of 6.8 keV/nm, with a peak kinetic energy per atom (at the centre of the spike) of 72.5 eV, and an average kinetic energy per atom (in the spike region) of 5.5 eV.
3.3.4 Charge stripping models

Delamination of the interface model

Delamination of the interface was modelled by removing the charges from atoms contained within a cylinder centred about the interface. These atoms were left with just their short range, mainly repulsive, potentials. The cylinder had radius 2 nm and extended 1 nm above and below the level of the interface between the two materials.

Charge stripping with recombination

The charge stripping model [127] takes the same cylindrical region used for the thermal spike model (see Figure 3.5) and removes the charge from all the atoms that are initially in this region (i.e. the Coulombic component of the potential energy function is removed). This models the swift heavy ion passing through the centre of the track and stripping electrons from all the ions close to its path. As a result of having their charge removed these atoms undergo repulsive interactions. All atoms in the system start the simulation with zero kinetic energy, i.e. the initial temperature is 0 K. As the simulation progresses the atoms that started with no charge recover their normal charge. At time $t$ we assume that the probability, $P_{\text{regain}}$, that an atom regains its charge is given by the following equation:

$$P_{\text{regain}} = 1 - \exp \left( -\ln 2 \times \frac{t}{t'} \right),$$

(3.3)

where $t'$ is the half life parameter. Atoms are assumed to regain their charge instantly. Since there is no theory sufficiently well developed to give a good handle on the value of the half life, $t'$ is treated as a variable parameter. Numerical experiments are carried out to investigate the effect of varying it.
Figure 3.7: Final image of the thermal spike model on system A showing a hillock has formed on the surface. Atoms are coloured by height between the surface and the top of the hillock.

3.4 MgO results

3.4.1 Thermal spike model

A thermal spike model with an electronic energy loss of 6.8 keV/nm was simulated on system A (Table 3.1), with the resulting surface topography shown in Figure 3.7. The system size was chosen to be as large as possible so that results could be obtained in a reasonable time, and the energy loss was chosen so that the simulation could be contained within the system we were using. To relate this to the kinetic energy of a swift heavy ion we refer to the paper by Skuratov et al [116], where a Kr$^{27+}$ ion with kinetic energy of 245 MeV has an electronic energy loss of 15.8 keV/nm in MgO. The single hillock that has formed has diameter 4.2 nm and height 2.3 nm. Figure 3.8 shows the average temperature in the system as a function of distance from the centre of the thermal spike region. Although initially the temperature outside the thermal spike region is 0 K, a wave of kinetic energy quickly forms and spreads through the lattice to the boundaries. The wave was calculated to be travelling at a speed of approximately 17,000 m/s. A similar wave was seen in all the simulations we ran. The wave is travelling significantly faster than the experimentally calculated speed of sound in MgO (9,150 m/s longitudinal and 6,620 m/s transverse [128]).

Following this initial simulation a further thermal spike simulation was carried out on system B, a system twice as deep as the original one. We again saw the formation of a single hillock of almost identical proportions – diameter 4.3 nm and height 2.3 nm – showing that
3.4. MGO RESULTS

Figure 3.8: The average temperature within the lattice as a function of distance from the centre of the thermal spike cylinder, as the simulation progresses, for system A. Note the wave of kinetic energy travelling away from the spike region. (a) shows the initial distribution of energy in the thermal spike. The system boundary is located at 8.5 nm. The thermostat is in effect from 6.5 nm removing excess energy from the system.
Figure 3.9: Cross section of the system B MgO thermal spike simulation at 32.3 ps, showing some areas of damage in the thermal spike region and the crystalline structure of the hillock. Red spheres represent O atoms, silver spheres represent Mg atoms.

lattice depth appears to have little effect on the resulting surface structure. The wave of kinetic energy travelling away from the spike was calculated to be the same as for the smaller system (17,000 m/s). There was a 20% difference in sputtering yield – during the system A simulation 981 atoms were sputtered whereas 1,190 atoms were sputtered in the system B simulation.

Figure 3.9 shows a cross section of the lattice in the system B simulation after 32.3 ps. Here we can see some defective regions still exist in the initial thermal spike region although most of the lattice is crystalline, with the same simple cubic (rocksalt) structure as the original system.

### 3.4.2 Charge stripping model

Charge stripping models with half life parameter values of 50, 100 and 500 fs were carried out on system A. Final images of the surfaces in each case can be seen in Figure 3.10. As the half life increases the height of the hillock also increases. This is due to the fact that atoms remain without charge (i.e. in an excited state and thus purely repulsive) for longer in the larger half life simulations. Figure 3.11 shows the relative density in the initial track region and the entire lattice for the simulation with a half life parameter of 50 fs. We see
Figure 3.10: Images of the final surfaces in simulations of the electron stripping with recombination model on MgO for different half life parameter values. Atoms are coloured by height between the surface and the peak of the hillock.

Figure 3.11: The relative densities in the ion track region and the entire lattice against time, for the 50 fs half life MgO simulation.
a large initial drop in the density within the track region, as atoms push out of the region. The density then increases as some of the atoms return. The drop in density in the entire lattice is due to atoms being ejected from the lattice.

Graphs showing hillock height and sputtering yield against half life are given in Figure 3.12. We see an approximate linear correlation in both cases. This can be compared to the experimental study by Skuratov et al [116] where they showed that hillock height varies linearly with electronic energy loss.

3.5 HfO$_2$ - MgO interface results

3.5.1 Bombarding the MgO free surface

Cluster impacts

Cluster impacts across the MgO surface were performed using a 19 atom argon cluster on models C and D from Table 3.1. Total kinetic energy given to the cluster was 4 keV (approximately 211 eV per atom).

Figure 3.13(a) shows the total number of “defects” plotted against time for the latter case, and shows multiple peaks in the total number of “defects”. Here a defect is identified in terms of an atom being displaced from a site in the original lattice. These multiple peaks
3.5. HFO\textsubscript{2} - MGO INTERFACE RESULTS

Figure 3.13: Total number of defects plotted against time for the 19 atom, 4 keV argon cluster impact and a 2 keV single gold atom impact across the MgO free surface.

were also present in the case of the smaller system. The small initial peak corresponds to the argon cluster impacting the surface of the system while the larger, second peak occurs when the initial cascade reaches the interface.

Figure 3.14(a) shows displaced atoms after 750 fs and although the argon cluster has not penetrated far, atoms at the interface have been displaced. The second image, Figure 3.14(b), shows that a large number of atoms in the MgO layer have been displaced (between the surface and the interface), with only a small section of the HfO\textsubscript{2} layer effected. Figure 3.14(c) shows that by 3 ps many displaced atoms have returned to their initial positions. However, after 3.4 ps (Figure 3.14(d)) there are further displacements at the interface which again spreads through the MgO layer to the surface. The energy from the cascade is essentially trapped in the MgO layer with nowhere to go. It thus oscillates across the layer, periodically initiating distortion to the interface. A similar effect has been observed in the case of cluster impacts on graphite [129], where the graphite structure allowed surface ripples to occur, rather than a vibration in the entire layer. One reason this could mainly be occurring in the MgO layer is the large difference in mass between magnesium and hafnium – the mass of hafnium is approximately seven times that of magnesium. Thus the magnesium atoms are much more likely to be displaced than hafnium atoms.
Figure 3.14: 19 atom, 4 keV argon cluster impact across MgO free surface (lattice B). Atoms displaced more than 1 Å are shown. In this and subsequent figures red spheres are oxygen, silver spheres are magnesium, gold spheres are hafnium and green spheres are argon.

**Single atom impacts**

A single gold atom impact across the MgO surface with 2 keV kinetic energy was simulated using model C (Table 3.1). In this case (Figure 3.13(b)) there is a small initial peak in the total number of “defects” followed by a larger second peak. This is different to what is observed when cascades are initiated in a bulk material, where a single peak is observed due to an initial thermal spike which gradually subsides.

Figure 3.15(a) shows the displaced atoms at the end of a typical single atom impact simulation. There is a trail of displaced atoms to the interface along the ion path but Figure 3.15(b) shows that the majority of these displaced atoms are not defects, having relaxed to adjacent lattice sites. The surface was disturbed but for this trajectory no atoms were sputtered and at this energy a few defects were formed at the interface but none in the hafnia substrate.
3.5. HfO$_2$ - MGO INTERFACE RESULTS

3.5.2 Bombarding the HfO$_2$ free surface

Single atom impacts

Single gold atom impacts across the HfO$_2$ surface were simulated with 4 and 8 keV kinetic energies on system E (Table 3.1). Only a few defects form in the bulk material after the ballistic phase of the cascade. After the initial 4 keV impact further impacts onto the same system were performed across random locations on a central section of the free surface. More defects formed around the interface and the surface regions began to amorphise. However no craters were seen to be forming in the surface and there were no sputtered atoms.

Cluster impacts

Initially the same 19 atom argon cluster (as used in the previous MgO free surface simulation) was chosen to bombard the HfO$_2$ surface. However over a range of bombardment energies a large number of the argon atoms were reflected from the surface. Therefore a heavier 55 atom gold cluster with 20 keV total kinetic energy (approximately 354 eV per atom) was used instead. Model F was used for this simulation (Table 3.1). Results obtained following

Figure 3.15: Displaced atoms and defects present 4 ps after a 2 keV gold atom (coloured blue) impact across the MgO surface. Cubes represent empty lattice sites.
Bombardment by the gold cluster are shown in Figure 3.16, with the first image showing the initial layout of the interface. After 600 fs the cluster has reached the interface, causing distortion of the interface and compression in the MgO. A crater has formed in the wake of the cluster although no sputtering was observed: instead the hafnia around the crater has been compressed away and upwards, raising the level of the surface around the crater. Also seen in the MgO is a distorted region below where the cluster hit the interface. The final image (Figure 3.16(c)) after 5 ps shows that the distorted region in the MgO layer has recovered and the crater partially filled.
3.5. HfO\textsubscript{2} - MGO INTERFACE RESULTS

Figure 3.17 shows a top down view of a portion of the HfO\textsubscript{2} free surface after two further (three in total) 55 atom, 20 keV gold cluster impacts have been simulated. The colours represent depth between the surface and anything above it (red), and the interface and anything below it (blue). Craters have formed and reach down to the interface in one case. However it would appear that the craters are too small to observe any obvious structures forming within them.

3.5.3 Thermal spike model

A thermal spike model with electronic energy loss of 6.8 keV/nm was simulated on the HfO\textsubscript{2}-MgO interface (system F). The result was the formation of a hillock on the surface with height of 3.4 nm and diameter 8.9 nm. However no crater was seen to form in the surface.

Figure 3.18 shows graphs of the temperature in the lattice as a function of distance from the centre of the thermal spike region. We see a wave of kinetic energy quickly spreading from the spike region to the rest of the lattice. This initial wave was calculated to be travelling at a speed of approximately 20,000 m/s through the material.

3.5.4 Delamination of the interface

Delamination of the interface was modelled using system D (Table 3.1). Charges were removed from approximately 2,400 atoms out of nearly 300,000 atoms, from a cylinder of radius and height 2 nm centered about the interface.

Figure 3.19(a) shows this model 8 ps after the simulation began. Initially the surface atoms stop the atoms in the centre of the lattice escaping, forming a large mound in the surface. Eventually the atoms with only repulsive interactions break out of the mound and explode out of the lattice. The surface atoms that formed the mound fall back onto the surface around the large crater that has formed as a result of the neutrally charged atoms bursting out of the system. This can be seen in Figure 3.19(b) which shows atoms coloured
Figure 3.18: The average temperature within the lattice as a function of distance from the centre of the thermal spike, at different times of the simulation. Note the wave of kinetic energy travelling away from the centre of the spike. (a) shows the initial distribution of energy in the thermal spike region. The system’s boundary is at 8.25 nm with the thermostat in use from 6.25 nm.
3.5. HFO$_{2}$ - MGO INTERFACE RESULTS

Figure 3.19: Images from the delamination model showing (a) displaced atoms, and (b) the crater in the surface where atoms are coloured by height (in Å) between the interface (blue) and the surface (red). The network structure on the surface is a reconstruction which forms as a result of removing half the Hf atoms to make the surface stable.

by height between the interface and anything below it (blue), and the surface and anything above it (red). The diameter of the crater, measured at the surface, is slightly larger than the diameter of the cylinder used to remove the charges from the atoms: the cylinder had diameter 4 nm whereas the diameter of the crater (at the surface) is approximately 5.5 nm. Towards its base the crater becomes slightly narrower but there is no evidence of a raised central region, as observed in experiments. An interesting feature of these interface simulations is the surface reconstruction network that appears on the free surface of the lattice, as shown in Figure 3.19(b). This reconstruction occurs due to the method for creating a stable free surface, in which half the Hf atoms are removed from the surface.

3.5.5 Charge stripping model

Charge stripping with recombination models were carried out for half life parameter values of 50, 100 and 500 fs (see Equation 3.3), on system F (Table 3.1). Images of the final surface are shown in Figure 3.20. The hillocks that are formed grow in height and diameter as the half life increases.
Figure 3.20: Images of the final surfaces in simulations of the electron stripping with recombination model on the HfO$_2$-MgO system, for different half life parameter values. Atoms are coloured by height between the surface and the peak of the hillock. Note the network structures of Hf atoms on the surface.

Figure 3.21 shows cross sectional images of the ion track during the 50 fs half life simulation. From this we can see how the system evolves during the simulation, and the development of the hillock on the surface and the ion track within the material. The first image shows the system near the beginning of the simulation and you can see that at this point the damage in the lattice is very localised to the path of the ion. There is evidence of sputtering at this stage with some individual atoms being ejected from the system. After 4 ps we see the state of system has changed significantly. MgO from the track region has started to force its way into the layer of hafnia. Although largely deformed, at this stage the hafnia layer still remains intact, forming a “cap” on the surface. Remarkably the damage still remains very localised to the track region around the path of the ion, particularly in the MgO layer. At this stage we do see some distortion of the interface due to the MgO layer swelling slightly. We also see small clusters of atoms being sputtered from the system at this time, rather than single atoms previously.

6.7 ps into the simulation (Figure 3.21(c)) we see chunks of the hafnia layer, along with some MgO, are breaking away from the system due to the pressure from the MgO region. Away from the ion track the system remains mostly unaffected and towards the bottom of the MgO region the width of the defective track has decreased. There is still some distortion of the interface throughout the system although away from the track region the hafnia seems to have recovered slightly. This is due to it being under less strain now that a section of it
Figure 3.21: Cross sectional images of the ion track in the charge stripping model with a half life value of 50 fs, showing the evolution of the system.
has broken away and it is no longer trying to hold in the MgO from pushing up through the layer (as this has forced its way out of the system now). Over the next 9 ps we see large chunks of hafnia and MgO breaking away from the system. By 15.9 ps we can see that the hafnia has again formed a “cap” over the MgO and you can see the hillock beginning to form on the surface. Atoms which were breaking away from the system may have regained their charges, causing them to fall back to the surface of the system forming the hillock. We see that the system, especially the MgO layer, has recovered a lot and the diameter of the damaged region (track) has reduced significantly.

Much later in the simulation, in Figure 3.21(e), we see the hafnia layer that was falling back to the surface, forming the hillock, has pushed the MgO back down towards its original layer. However the MgO still protrudes slightly into the hafnia layer in the vicinity of the ion track. Away from the ion track region the system remains undamaged, although some slight distortion of the interface is apparent. Within the track region, in the MgO layer, some voids have formed, notably a large one near the interface and some smaller ones towards the bottom of the layer. After 40 ps we see that the system has not changed much more. The void in the MgO layer at the interface is still present, as are the smaller ones towards the bottom of the layer. These “hollow tracks” have been observed in experimental work such as the one by Garrido et al [19]. Away from the ion track the interface remains intact.

Plotted in Figure 3.22 are the relative densities in the lattice (i.e. within the original dimensions of the system, so not including atoms on top of the surface) and the original track region (from which atoms had their charges removed). The graphs for each half life simulation follow the same trend. Initially there is a large drop in density in the track region, lasting for approximately 1 ps. During this period atoms push out radially from the track centre into the surrounding material causing the drop in density. As the half life parameter increases so does the magnitude of this initial drop in density, due to the higher temperature in the track region (see Figure 3.31). The 50 fs half life track drops to approximately 0.55 times its original density, while the 100 and 500 fs simulations drop to approximately 0.46
3.5. HFO\textsubscript{2} - MGO INTERFACE RESULTS

Figure 3.22: Graphs showing the relative densities of the track region and entire lattice, against time, for the interface charge stripping simulations.

(a) Half life 50 fs

(b) Half life 100 fs

(c) Half life 500 fs
and 0.34 times their original densities. The next stage involves a rise in the density of the track region, from around 1 ps to 2 ps. This is caused by atoms that pushed out of the track recoiling back to the track region. Then after 2 ps these energetic atoms in the track region start to push upwards, with the MgO layer putting a lot of strain on the hafnia layer and pushing it above the original surface height. This causes the large drop in density of the track region. There is a slight plateau, or even another small peak, in the density as the hafnia layer restrains the energetic particles from escaping. However once these particles force their way from the system the density in the track drops significantly. It continues to drop for a period of time depending on the half life parameter, with the 50 fs simulation reaching a minimum track density at approximately 5.5 ps (0.4 times its original density), while the 500 fs simulation attains its minimum track density after roughly 25 ps (0.1 times its original). After this the track densities rise as material that was partially ejected falls back into the track and also the material starts to recover in general. The drop in density of the entire system is a result of particles being ejected or pushed onto the surface.

Also plotted is the radial distribution of displaced atoms (see Figure 3.23) for the 50 fs half life simulation. We see that, as you would expect, initial displacements occur near the centre of the track. As the simulation progresses the peak number of displaced atoms occurs further from the centre of the track until a peak is reached between 6 and 6.5 nm from the track centre. This corresponds to atoms initially pushing away from the track centre (see initial drop in track density in Figure 3.22(a)). This peak then moves closer to the track...
Figure 3.24: The average temperature within the lattice as a function of distance from the centre of the ion track, as the 50 fs half life simulation progresses. Note the wave of kinetic energy travelling away from the track region. The boundary of the system occurs from 8.25 nm, with the thermostat in effect from 6.25 nm.

centre and the number of displaced atoms drops overall: by 40 ps the peak in the radial distribution of displaced atoms occurs between 4 and 4.5 nm from the track centre (the track radius was 2 nm).

The average temperature in the lattice as a function of radial distribution from the centre of the track is plotted in Figure 3.24 and can be compared to the thermal spike model in MgO (Figure 3.8). We see that the charge stripping model on the interface produces a similar effect to the thermal spike model on MgO. Initially a wave of kinetic energy originates from the track region (see Figure 3.24(a) after 20 fs). This wave quickly spreads away from the track region and by 500 fs it is close to the edge of the lattice. By 2 ps we see the wave has reached the edge of the lattice but is still much higher in the track region. In each
Table 3.2: The peak temperatures and cooling rates of the ion track for the different half life values, for the charge stripping model simulations. The initial cooling rate is the cooling rate during the first 5 ps after the peak, when the cooling is fastest. The overall cooling rate is up to the point at which the temperature plateaus.

<table>
<thead>
<tr>
<th>Half life (fs)</th>
<th>Time to peak temperature (fs)</th>
<th>Peak Initial cooling rate (K/s)</th>
<th>Cooling rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>50</td>
<td>36,000</td>
<td>$6.4 \times 10^{15}$</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>49,000</td>
<td>$8.7 \times 10^{15}$</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>89,000</td>
<td>$1.6 \times 10^{16}$</td>
</tr>
</tbody>
</table>

Figure 3.25: Graphs showing sputtering yield and hillock height against half life for the HfO$_2$-MgO interface electron stripping model simulations. The red line is the best linear fit.

Simulation the wave was calculated to be travelling at approximately 12,000 m/s. By 40 ps the temperature in the lattice is evenly spread throughout the system. Table 3.2 shows the information on the peak temperatures of the ion track regions for the different half life values, along with initial and overall cooling rates. We see that the peak temperature in the track region is reached quickly (within 100 fs). The initial cooling rate (over the first 5 ps) is high although the overall cooling rate up to the point at which the temperature levels off is lower. The cooling rate could be effected by the choice of time constant in the thermostat (we used $\tau = 1$ ps in Equation 2.33). The thermostat is situated towards the edge of the system, 6.25 nm from the centre of the ion track.

Graphs of the sputtering yield and hillock height against half life parameter are shown in Figure 3.25. We see that both the hillock height and sputtering yield increase linearly with half life (effectively the electronic stopping force of the ion), as we also found for the MgO simulations. This has been seen before, for example in the study by Bringa et al [130],
3.5. HFO\textsubscript{2} - MGO INTERFACE RESULTS

![Graphs showing the sputtering yield and hillock height against half life for the HFO\textsubscript{2}-MgO interface electron stripping model simulations on the larger system. The red line is the best linear fit.](image)

where they note that for high electronic stopping forces and a constant track radius the yield exhibits roughly linear dependence on the electronic stopping force.

### 3.5.6 Charge stripping model, larger system

A further set of simulations using the charge stripping model were carried out on the larger system G (Table 3.1). This system has a larger surface area but the same depth as before because we wanted to see if the surface area of the previous system was effecting the simulation. All other variables remained the same.

Figure 3.26 shows images of the surface of each system at the end of the simulations. We
see that in each case a hillock has formed on the surface. As the half life increases we see an increase in the height of the hillocks, although in this case the diameters remain roughly the same. The hillock heights against the half life parameter are plotted in Figure 3.27, along with the sputtering yields. In the case of the hillock heights we see good linear fit, as we have done in all the previous simulations. For the sputtering yield the linear fit is not so strong but does increase almost linearly with the half life parameter. However the statistics are poor due to the number of different parameter values simulated.

Cross sectional images of the lattice taken through the ion track are shown in Figure 3.28. At the end of the 100 fs half life simulation we observe some small voids forming in the track region. There is swelling at the surface and some MgO has pushed into the layer of HfO$_2$. Away from the ion track the lattice appears to have largely retained its crystal structure, particularly in the HfO$_2$ layer. Figure 3.28(b), taken at the end of the 500 fs half life simulation, shows a slice through the lattice. We observe a large void has formed in the MgO layer, reaching from the bottom of the lattice up to the interface, which has distorted. Away from the ion track the crystal structure is retained, although some distortion is evident in the MgO layer.

The relative densities of the ion track region and the entire lattice are plotted against
3.5. HFO$_2$ - MGO INTERFACE RESULTS

(a) Half life 50 fs

(b) Half life 100 fs

(c) Half life 500 fs

Figure 3.29: Graphs showing the relative densities of the track region and entire lattice, against time, for the interface charge stripping simulations on the larger system.
Figure 3.30: The average temperature within the lattice as a function of distance from the centre of the ion track, during the 500 fs half life simulation. Note the wave of kinetic energy travelling away from the track region. The boundary of the system occurs from 12.9 nm with the thermostat in effect from 10.9 nm, removing excess energy from the system.

Comparing these graphs to those for the simulations on the smaller system (Figure 3.22) we see that the lateral size of the system appears to have little effect on the density of the ion track region. The corresponding graphs have the same shape in each case, and peaks and basins occur at almost exactly the same levels, and at the same times.

Figure 3.30 shows the average temperature in the system as a function of distance from the centre of the ion track, during the 500 fs half life simulation. After 100 fs we see a peak in the temperature ($\approx 100,000$ K) within the ion track, which has yet to spread to the rest of the system. The second graph shows the progress the wave of kinetic energy is making through the system after 500 fs. The speed of the wave was calculated to be approximately 12,000 m/s. This was the same for each half life parameter value.

The average temperatures of the ion track region and the entire lattice are plotted against time in Figure 3.31. We see the temperature in the ion track peaks at the beginning of each simulation and then drops quickly until it levels off slightly hotter than the average temperature in the system. If the simulation were continued long enough the track region would eventually cool to the same temperature as the rest of the lattice. Corresponding values for peak temperatures and cooling rates are shown in Table 3.3. During the 50 fs
3.5. \( \text{HFO}_2 - \text{MGO INTERFACE RESULTS} \)

Figure 3.31: Graphs showing the average temperatures of the track region and entire lattice, against time, for the interface charge stripping simulations on the larger system.

(a) Half life 50 fs

(b) Half life 100 fs

(c) Half life 500 fs

Figure 3.32: The peak average temperature of the ion track against half life parameter value, for the charge stripping model simulations on the larger interface system. The red line is the linear best fit.
### Table 3.3: The peak temperatures and cooling rates of the ion track for the different half life values, for the charge stripping model on larger interface simulations. The initial cooling rate is the cooling rate during the first 5 ps after the peak, when the cooling is fastest. The overall cooling rate is up to the point at which the temperature plateaus.

<table>
<thead>
<tr>
<th>Half life (fs)</th>
<th>Time to peak temperature (fs)</th>
<th>Peak Initial cooling rate (K/s)</th>
<th>Overall cooling rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>50</td>
<td>35,000</td>
<td>$6.1 \times 10^{15}$</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>48,000</td>
<td>$8.6 \times 10^{15}$</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>90,000</td>
<td>$1.6 \times 10^{16}$</td>
</tr>
</tbody>
</table>

Half life simulation the peak temperature in the ion track occurs after 50 fs, and reaches a temperature of roughly 35,000 K. The initial cooling rate in the track region, over the first 5 ps following the peak temperature, is $6.1 \times 10^{15}$ K/s. When the temperature of the track region starts to level off (at around 2,900 K) the cooling rate is $2.2 \times 10^{15}$ K/s. The peak temperature in the ion track during the 100 fs half life simulation also occurs after 50 fs at a higher temperature of 48,000 K. The initial and overall cooling rates of the track are also higher than the 50 fs half life case. The trend continues for the 500 fs half life simulation. These figures agree with the work of Szenes [28], where the author notes the peak temperature in the track occurs soon after the ion impact ($< 10^{-12}$ s), and the track cools on the picosecond timescale at a rate in the region of $10^{15}$ to $10^{14}$ K/s. Figure 3.32 shows the peak average temperature of the ion track region during the simulation, for the different half life parameter values. The graph shows strong linear correlation.

### 3.5.7 Charge stripping model, larger system and track radius

A further set of simulations were performed with everything the same as the previous set except for a larger initial track radius of 3 nm (compared to 2 nm). Once again these simulations were carried out for half life parameter values of 50, 100 and 500 fs.

Images of the surface following each simulation are shown in Figure 3.33. We see that in the case of the 50 and 100 fs half life simulations (Figures 3.33(a) and 3.33(b)) a single hillock forms on the surface, as we have observed in the previous simulations. However following the 500 fs half life simulation we see a crater has formed in the surface around which a large
3.5. HFO\textsubscript{2} - MGO INTERFACE RESULTS

Figure 3.33: Images of the final surfaces in simulations of the electron stripping with recombination model on the larger HFO\textsubscript{2}-MgO system and larger track radius. Atoms are coloured by height between the surface and the peak of the hillock. For reference, the area of the surface is 25.8 × 25.8 nm\textsuperscript{2}.

(a) Half life 50 fs  
(b) Half life 100 fs  
(c) Half life 500 fs

Figure 3.34: Viewing a slice through the lattice, taken at the end of the 500 fs half life simulation on the larger system with larger initial track radius. Notice the large void at the base of the lattice, which reaches all the way to the surface.

Figure 3.35: Graph showing the sputtering yield against half life parameter, for the larger track radius and system simulations. The red line is the linear best fit.
Table 3.4: The peak temperatures and cooling rates of the ion track for the different half life values, for the charge stripping model on larger interface simulations with the larger initial track radius. The initial cooling rate is the cooling rate during the first 5 ps after the peak, when the cooling is fastest. The overall cooling rate is up to the point at which the temperature plateaus.

<table>
<thead>
<tr>
<th>Half life (fs)</th>
<th>Time to peak temperature (fs)</th>
<th>Peak temperature (K)</th>
<th>Initial cooling rate (K/s)</th>
<th>Cooling rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>70</td>
<td>33,000</td>
<td>$5.4 \times 10^{15}$</td>
<td>$1.9 \times 10^{15}$</td>
</tr>
<tr>
<td>100</td>
<td>90</td>
<td>49,200</td>
<td>$8.3 \times 10^{15}$</td>
<td>$2.7 \times 10^{15}$</td>
</tr>
<tr>
<td>500</td>
<td>90</td>
<td>94,000</td>
<td>$1.7 \times 10^{16}$</td>
<td>$4.9 \times 10^{15}$</td>
</tr>
</tbody>
</table>

A large void has formed at the base of the lattice. The void reaches all the way to the surface. This is the first simulation where a hollow region has existed reaching all the way through the lattice, as in previous simulations the ejected matter that did not have enough energy to fully escape the surface, fell back to the surface and formed a cap over any hollow regions. The diameters of the hillocks were 6.8, 11.4 and 17.5 nm for the 50, 100 and 500 fs half life simulations respectively. The corresponding heights are 2.7, 5.5 and 4 nm. Clearly there is not a linear increase in hillock as half life increases, as we have seen in all the previous simulations. However this can be explained by the fact that in the 500 fs half life simulation we did not observe the formation of a “normal” hillock. Instead we saw one form with a crater in the centre reaching to the bottom of the lattice. Thus it appears a lot more atoms were sputtered, rather than forming a hillock. The sputtering yield against half life parameter is shown in Figure 3.35, where once again we observe strong linear correlation.

Figure 3.36 shows graphs of the relative densities of the entire lattice and the ion track region against time, for the different half life parameter values. The graphs for the 50 and 100 fs parameters have the same shape as for the 2 nm track radius simulations, although the densities of the track regions fall slightly lower. The relative density of the track region in the 500 fs half life simulation has the same initial shape as in previous simulation but then the relative density drops to nearly zero as a void forms in the track region (shown in Figure 3.34). Towards the end of the simulation the density increases slightly as some atoms return to this region.
Figure 3.36: Graphs showing the relative densities of the track region and entire lattice, against time, for the interface charge stripping simulations on the larger system with larger initial track radius.
Figure 3.37: The average temperature within the lattice as a function of distance from the centre of the ion track, during the 100 fs half life simulation on the larger system with larger initial track radius. Note the wave of kinetic energy travelling away from the track region. The boundary of the system occurs from 12.9 nm with the thermostat in effect from 10.9 nm, removing excess energy from the system.

As in the other simulations we see a wave of kinetic energy travelling away from the track region. This wave is shown in Figure 3.37 for the half life 100 fs simulation. The wave speeds were calculated to be between 11,500 and 12,000 m/s for the different half life values. Figure 3.38 shows the average temperature in the entire lattice and the ion track region against time, for the different half life values. The peak temperatures in the track region are similar to the track with the smaller radius. Table 3.4 has data on the peak temperatures and cooling rates for the different simulations. The numbers are similar to the simulations with the smaller initial track radius, which seems to suggest that initial track radius and system size do not effect the peak temperature attained in the track, or the cooling rates.

3.6 Conclusions

These results give an insight into the modelling of radiation effects, specifically swift heavy ion bombardment, in particular on a HfO$_2$–MgO interface system. The interface system was successfully created with either the HfO$_2$ or MgO layer free using the method described
3.6. CONCLUSIONS

(a) Half life 50 fs  

(b) Half life 100 fs  

(c) Half life 500 fs  

Figure 3.38: Graphs showing the average temperatures of the track region and entire lattice, against time, for the interface charge stripping simulations on the larger system with larger initial track radius.
in this chapter. Initially single atom and cluster bombardment across both surfaces was simulated in an attempt to produce craters in the surface of the material. Although this was unsuccessful we did demonstrate the resistance to damage of this interface system.

An interesting feature that was seen when bombarding the MgO free surface was long time scale vibrations in the entire layer of MgO. This was not observed in the HfO$_2$ layer, probably due to the large difference in mass between Hf ($\approx 178$ amu) and Mg ($\approx 24$ amu), meaning that the Mg atoms are much more likely to be displaced that the Hf. Single atom bombardment across either surface resulted in very little damage in the material. Multiple cluster (55 Au atoms, 20 keV) bombardment of the HfO$_2$ free surface resulted in formation of a crater reaching down to the interface. However this also demonstrated the interface’s ability to heal as the interface recovered from some initial distortion resulting from the impact. We also noticed craters partially filling as the simulation progressed. An observation made during these single atom and cluster bombardment simulations was that there was little or no sputtering.

Two main models for swift heavy ion bombardment were presented: a thermal spike model and a charge stripping model (including a delamination of the interface model and a charge stripping with recombination model). Simulations using these models were carried out on the HfO$_2$-MgO interface system, and also on MgO. The MgO thermal spike model showed the formation of a hillock on the surface and an ion track in the material, around the path of the swift heavy ion. These are both features that are seen experimentally [19, 116]. We also showed how a wave of kinetic energy (temperature) travels from the initial thermal spike region to the edge of the system. A second thermal spike simulation was performed on a system of twice the depth of the original one and it was shown that this increase in depth had little or no effect on the size of the resulting surface structure (hillock). We saw that most of the lattice was crystalline, with some defective regions in the ion track, with the structure of the hillock also crystalline.

The charge stripping with recombination models on the MgO system also resulted in the
formation of ion tracks around the path of the ion, and a hillock on the surface. We showed that by increasing the half life parameter in our model (effectively increasing the electronic stopping force of the swift heavy ion) the height of the resulting hillock would also increase, with an almost linear relationship. This relationship was seen in the experimental study by Skuratov et al [116]. We also calculated the sputtering yield as a function of half life parameter and showed that there is also a linear relationship here. This has also been seen in the work by Bringa et al [130], comparing MD simulations of a spike to a traditional thermal spike, and also a hybrid model. Both the hybrid and MD models showed linear correspondence.

A thermal spike model on the HfO$_2$-MgO interface was simulated and, as in the MgO thermal spike, produced a hillock and ion track, but no crater. An attempt to model delamination of the interface was performed and resulted in the formation of a crater but without a raised central region, as seen in the experiments mentioned earlier. Following this, three charge stripping with recombination models were carried on the interface, using half life parameters of 50, 100 and 500 fs. As in the MgO simulations, and the literature, we showed there was a strong linear relationship between half life (effectively electronic stopping power) and sputter yield. Once again there was also a linear relationship between hillock height and half life parameter.

The process by which the hillock is created was described for the half life 50 fs simulation. We saw that initially atoms push out radially from the track region, then recoil and push upwards. The HfO$_2$ layer forms a cap over the MgO (pushing upwards) that eventually is broken, with large amounts of atoms being ejected from the system. As atoms regain their charges they are attracted back to the lattice more and many atoms fall back onto the surface, forming a hillock on the surface. Due to the amount of atoms that were sputtered out of the system voids were found in the track region, which was much less dense than the rest of the lattice (and its original density).
Chapter 4

Bullet impacts on SiC

4.1 Introduction

Silicon carbide (SiC), a hard ceramic, has many important applications in the modern day including in the electronics industry, as an abrasive and in high wear environments [131]. Another use of SiC is in military applications, for example armour plating, due to the fact it is generally strong in compression and after failure. For this reason there continues to be a lot of interest in the reaction of this material to high speed ballistic impacts [131, 132, 133, 134].

Experimental studies, such as the one by Vogler et al [131], have investigated the strength of SiC under impact. They found that the strength behaviour of SiC in their impact experiments was “metal-like” in character, implying the development of significant plastic deformation such as the formation of dislocations. The experimental study by Leavy et al [134] observes large cracks forming on the surface around the bullet impact site.

Johnson summarises a range of numerical algorithms and models for high velocity impacts in his paper [133], which were based on a finite element approach, using a more sophisticated meshless particle method. An advantage of these types of simulation is the ability to model realistically sized systems for comparison with experimental data. In their paper Branicio et al perform a large scale MD simulation of hypervelocity (15 km/s) projectile impacts on
AlN. They summarise the advantages of molecular dynamics (MD) simulations over finite elements methods: by using reliable interatomic potentials, microscopic material properties such as nonlinear and plastic deformation can be studied [135]. The limitation of MD is the size of the systems that can be modelled – much smaller than those used experimentally – and also the time scales that can be achieved.

In this chapter a model, and corresponding results, are presented for simulating bullet impacts on SiC.

4.2 Methodology

4.2.1 The bullet

Initially the bullet was modelled using a sphere of Ar atoms. In order to model the momentum a bullet would have on impact we chose to hold the atoms in the sphere fixed, so they can only move with the velocity we give them. Thus the cluster of atoms is forced into the lattice in a similar way to molecular dynamics simulations of nanoindentation (without the springs) [136]. Using this model the bullet penetrated the target surface but we found that rather than being totally repelled by the bullet atoms, some Si and C atoms found their way in between the Ar atoms in the cluster. In order to stop this from happening our final model represented the bullet by a single hard sphere with a controlled velocity. This sphere had a purely repulsive ZBL interaction with the target SiC atoms. Input parameters to the model were:

- bullet radius,
- bullet initial speed,
- target depth in the substrate.

The bullet’s velocity was set at the initial speed up to the point at which it contacted the target surface. At this point the speed was reduced linearly until the bullet came to rest at
4.2. METHODOLOGY

(a) 4H

(b) 6H

Figure 4.1: Images showing the different SiC structures used in the simulations.

<table>
<thead>
<tr>
<th></th>
<th>Number of atoms</th>
<th>Structure</th>
<th>Lattice volume (nm$^3$)</th>
<th>Thermal layer (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4,097,737</td>
<td>6H</td>
<td>34.4 × 34.4 × 34.5</td>
<td>1.5</td>
</tr>
<tr>
<td>B</td>
<td>4,291,138</td>
<td>4H</td>
<td>35.0 × 35.0 × 35.0</td>
<td>1.5</td>
</tr>
<tr>
<td>C</td>
<td>16,333,641</td>
<td>6H</td>
<td>68.8 × 34.4 × 69.0</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4.1: The SiC systems that were used for the bullet impact simulations. The “thermal layer” column indicates the distance the thermostat extends within the fixed boundaries.

its target depth. In the model it is assumed that atoms in the substrate have no effect on the motion of the bullet.

4.2.2 Computational method

A substrate consisting of either 6H or 4H SiC was constructed – the different SiC structures are shown in Figure 4.1. In both structures the chemical bonds between Si and C atoms are identical and tetrahedrally coordinated, whereas the stacking sequence differs [137]. The different systems that were used for these simulations are shown in Table 4.1. The top surface, which the bullet will hit, was left free and all other surfaces were held fixed. Inside each fixed boundary a thermal layer, held at 0 K, was used to remove excess energy from the
4.3 Results

4.3.1 Preliminary calculations

Some properties of the different structures of SiC were calculated and compared to other work, to show that the potential energy function describes the behaviour of the material in a realistic way. The calculated values are shown in Table 4.2. These values were obtained by

Table 4.2: Structural properties of 4H and 6H SiC calculated in this work and compared to values calculated elsewhere. $E_0$ is the equilibrium energy per atom, $V_0$ is the equilibrium atomic volume, $B_0$ is the equilibrium bulk modulus and $B'_0$ is the pressure derivative of the bulk modulus.

<table>
<thead>
<tr>
<th>Property</th>
<th>4H This work</th>
<th>Elsewhere</th>
<th>6H This work</th>
<th>Elsewhere</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$ (eV/atom)</td>
<td>-6.17</td>
<td>-</td>
<td>-6.17</td>
<td>-</td>
</tr>
<tr>
<td>$V_0$ (Å³/atom)</td>
<td>10.08</td>
<td>-</td>
<td>10.08</td>
<td>-</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td>224</td>
<td>220 [138]</td>
<td>224</td>
<td>220 [138]</td>
</tr>
<tr>
<td>$B'_0$</td>
<td>4.09</td>
<td>-</td>
<td>4.09</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.2: Change in the energy per atom for the 6H SiC system as the lattice is uniformly distorted during the bulk modulus calculation. The parameter $\delta$ is the percentage increase in lattice spacing. The red circles are the calculated data and the blue line is the Stineman interpolation.

The system (introduced by the bullet). The Berendsen thermostat was used with a time constant $\tau = 1$ ps (Equation 2.33). The initial temperature of the substrate was 0 K. The bullet was initially placed far enough from the surface such that there was no interaction between it and the surface atoms.
uniformly expanding and contracting the system, giving us values for bulk energies against volumes per atom (shown in Figure 4.2 for the 6H case). We then fit these values, using a least squares method, to the Murnaghan equation of state [139]. The calculated values for the bulk modulus of both the 4H and 6H systems are close to those found in the literature. This is important when calculating results such as the speed of waves through the material.

4.3.2 6H SiC at 1,000 m/s

A bullet impact simulation was carried out on a 6H SiC system (A from Table 4.1) containing just over 4 million atoms. The bullet was given a radius of 4 nm and its penetration depth was set to 17 nm (approximately half way into the lattice). The initial speed of the bullet was 1,000 m/s. A time of 120 ps was simulated.

Figure 4.3 shows atoms that were displaced from their original positions by more than 1.3 Å, at different points in the simulation. Figure 4.3(a) shows the system as the bullet initially penetrates the substrate. We see a large number of displaced atoms originating from the point of impact and spreading in all directions through the material. The arrows indicate a wave of displacement moving across the surface. In the second image, 2.5 ps later, we see the number of displaced atoms has increased. The small wave of displaced atoms spreading across the surface has reached the edge of the system although the bulk of the displaced atoms are still far from the edges of the system. Prior to this point we also observe atoms being thrown up onto the surface around the bullet. The final image (Figure 4.3(c)) shows the system after 120 ps. This image shows a large number of displaced atoms around the path of the bullet. Atoms at the surface are also displaced from their original positions. Plotted in Figure 4.4 is the number of displaced atoms against time. The number of displaced atoms rises sharply as the bullet impacts the surface. The graph then oscillates for a period until it reaches a plateau. At the end of the simulation approximately 37 % of the atoms are displaced from their original position by more than 1.3 Å.

Images taken of a cross section along the path of the bullet are shown in Figure 4.5.
Figure 4.3: Images showing displaced atoms at different points of the simulation. Black coloured atoms are carbon, yellow silicon. The arrows in (a) indicate the wave of displacement travelling across the surface.
Figure 4.4: A graph showing the number of displaced atoms against time during the 1,000 m/s bullet on 6H SiC simulation.

Figure 4.5: Cross sectional images of the 1,000 m/s bullet on 6H SiC.
The first image shows the state of the system before the bullet hits the surface, showing the perfect crystal structure of the lattice at this point. 2.5 ps later we see the bullet starting to penetrate the surface and there is distortion in the layers close to the surface. The final image shows the bullet at its target depth in the material. There is a clear track of damage left in the path and close proximity of the bullet. However away from the bullet track minimal damage is observed.

Figure 4.6 shows the same cross section from a different angle. The first image, taken after 2 ps, shows the bullet just after it has hit the surface. We see a wave of damage spreading radially from the bullet across the surface. The second image shows the system later in the simulation. At this point the bullet has penetrated far into the material and a cap has formed over its entry point. A small hollow region was observed directly behind the bullet.

A cross section of the system looking down at the $x, z$ plane is shown in Figure 4.7 and shows the damage left in the wake of the bullet. A clearly defined region in the centre of the lattice, where the bullet passed through, shows damage. The rest of the lattice appears to have retained its crystal structure although there is the hint of some distortion. This distortion is visible in the “rings” around the defective region, indicating there is a slight
4.3. RESULTS

Figure 4.7: A cross section of a section of the lattice the bullet has passed through. Note the clearly defined region of damage around the path of the bullet. Also note the distortion in the crystal structure characterised by the “rings” around the damaged region. The dimensions of the system as we look at it are $34.4 \times 34.5 \text{ nm}^2$.

Figure 4.8: Relative densities of the entire system and the bullet track region against time.

ripple in the layers around the path of the bullet. The track left by the bullet is an amorphous, lower density region and has a diameter of approximately 10.4 nm (the diameter of the bullet was 8 nm).

Figure 4.8 shows the relative densities of the entire lattice and the bullet track region, against time. As expected we see a large drop in density in the bullet region when the bullet impacts the surface, dropping as far as 60 % of its original density. Over time this region recovers and its density stabilises at around 74 %. The drop in density in the entire lattice is due to atoms being sputtered and also by atoms being thrown up onto the surface.
Figure 4.9: An image of the largest cluster (318 atoms) present after 120 ps.

Figure 4.10: Images of two medium sized clusters present after 120 ps.

(a) 88 atoms  
(b) 53 atoms
4.3. RESULTS

The total number of atoms ejected from the lattice after 120 ps was 2,846. Of these, 375 were lone atoms while the rest formed clusters of 2 or more atoms (an average of 5.3 atoms per cluster). There were only 6 clusters containing more than 20 atoms. Figure 4.9 shows the image of a cluster of atoms that was ejected from the system. The image was taken at 120 ps and was the largest cluster present at that time. The cluster contained 318 atoms (168 C and 150 Si) and was travelling at a speed of 470 m/s. The cluster had a total kinetic energy of 188 eV (0.59 eV per atom) and a total potential energy of $-1,455$ eV ($-4.6$ eV per atom). The kinetic energy of the cluster can be broken down into the kinetic energy of the centre of mass (7.17 eV) and the angular kinetic energy (123.2 eV), leaving an internal vibrational energy of 57.5 eV. The temperature of the cluster was calculated to be 1,399 K (the melting point of SiC is approximately 3,000 K). Two of the next largest clusters are shown in Figure 4.36. In Figure 4.10(a) is an 88 atom (47 C and 41 Si) cluster. This cluster had a total potential energy of $-403.6$ eV ($-4.6$ eV per atom) and total kinetic energy of 55.4 eV (0.63 eV per atom), of which 6.7 eV is the kinetic energy of the centre of mass, 33.1 eV is angular kinetic energy and 15.6 eV is internal vibrational energy. The cluster was travelling at a speed of 862 m/s and had a temperature of 1,374 K. Figure 4.10(b) shows a cluster containing 53 atoms (29 C, 24 Si). This cluster had a total potential energy of $-279.8$ eV ($-5.3$ eV per atom). The total kinetic energy was 6.8 eV (0.13 eV per atom) of which 0.2 eV is the kinetic energy of the centre of mass, 4.1 eV is angular kinetic energy and 2.6 eV is internal vibrational energy. The cluster was travelling at a speed of 189 m/s and had a temperature of 372 K.

Figure 4.11 shows the average temperature in the entire system and the bullet track region against time. We see a sharp increase in the temperature of the bullet region as the bullet impacts the surface, peaking at approximately 4,500 K. This peak occurs early in the simulation, after roughly 6 ps. Then, as the speed of the bullet decreases and it moves further into the material, the temperature in this region drops significantly to about 1,200 K (120 ps). The temperature of the entire system increases to around 800 K by 120 ps. In
Figure 4.11: Average temperature in the entire system and the bullet track against time.

(a) 0.4 ps  
(b) 1.2 ps  
(c) 3.6 ps  
(d) 120 ps

Figure 4.12: Graphs showing the average temperature in the lattice as a function of distance from the bullet.
Figure 4.12 graphs showing the average temperature in the lattice as a function of distance from the centre of the bullet are displayed. In the first graph (Figure 4.12(a)), after 0.4 ps, we see a sharp spike in the temperature of atoms close to the edge of the bullet reaching approximately 700 K at this point. The rest of the lattice is at, or close to, 0 K. The second graph, at 1.2 ps, shows this sharp spike (up to approximately 4,000 K) at very close range to the edge of the bullet. We see a wave of temperature (kinetic energy) starting to move away from the bullet although the peak drops quickly, with the average temperature dropping to under 10 K at distances of 8 nm or more from the edge of the bullet. After 3.6 ps (Figure 4.12(c)) the wave of kinetic energy has progressed towards the edge of the lattice and the peak of the spike in temperature at close range to the edge of the bullet has rise to approximately 8,000 K. At a distance of 8 nm from the edge of the bullet the temperature has dropped to 100 K which shows the temperature spike is short ranged. The final graph shows the temperature in the system has begun to level off and the spike is no longer visible at the edge of the bullet. The peak has dropped to just over 1,000 K and is a similar temperature towards the edge of the lattice. The speed of the wave of kinetic energy originating from the point of impact of the bullet was calculated to be approximately 6,000 m/s. This wave can be observed in the images of displaced atoms shown earlier (Figure 4.3(a)) and is indicated by the arrows. For reference the experimentally measured longitudinal speed of sound in SiC is roughly 13,000 m/s and the shear speed of sound is approximately 7,300 m/s [140].

The image in Figure 4.13 shows “slipped” atoms at the end of the simulation, corresponding to dislocations. However there was no evidence of any dislocations forming during this simulation.

4.3.3 4H SiC at 1,000 m/s

A simulation was then carried out using the 4H system B from Table 4.1, containing 4.3 million atoms and with similar dimensions to the previous 6H system. Identical parameters were used for this model as the previous 6H one: an initial bullet speed of 1,000 m/s, bullet
radius of 4 nm and penetration depth of 17 nm. A time of 120 ps was simulated.

Figure 4.14 shows snapshots of displaced atoms at different simulation times. The first image, taken after 2 ps, shows the system shortly after the bullet has contacted the surface. We see, as with the 6H simulation, a large number of displaced atoms originating from the point of impact. The shape these atoms take is different to the 6H simulation as a result of the different crystal structure. After 5.2 ps (Figure 4.14(b)) this wave of displaced atoms is pushing further from the point of impact as a wave of kinetic energy surges through the system. The different crystal structure is even more apparent in this image. We also see atoms being thrown up onto the surface around the bullet. This flow of material around the projectile and out of the lattice, due to the high temperature in this region, is seen experimentally [132]. Later in the simulation, in Figure 4.14(c), the bullet has pushed further into the lattice, causing an increase in the number of displaced atoms. A large number of atoms have been thrown up onto the surface, forming a cap over the bullets entry point into the material. After 120 ps we see a large number of atoms still displaced around the path of the bullet. The atoms thrown onto the surface have a square shape indicative of the crystal structure. Figure 4.15 shows the number of displaced atoms against time. Here we see the number increase sharply at the initial impact and continue to rise while oscillating slightly. The number eventually decreases slightly and levels off as the bullet reaches its penetration
4.3. RESULTS

(a) 2 ps
(b) 5.2 ps
(c) 17.2 ps
(d) 120 ps

Figure 4.14: Images showing displaced atoms at different points of the 1,000 m/s on 4H simulation. Black coloured atoms are carbon, yellow silicon.
depth. At the end of the simulation approximately 27% of the atoms are displaced from their original positions. This is 10% less than in the previous 6H SiC simulation. Ab initio calculations have indicated that the 4H structure is more stable than the 6H (and 3C) polytypes [141].

Figure 4.16 shows images of the free surface during the bullet impact. The first image shows the structure of the surface before the bullet hits it. The second image, taken after 8 ps of simulation time, shows the bullet entering the material. A large number of atoms are thrown up onto the surface at this point. In Figure 4.16(c) we see the debris that was thrown up onto the surface is forming a cap over the path of the bullet, which has pushed further into the material. The shape of the cap is square as a result of the cubic-like 4H crystal structure. After 120 ps of the simulation the cap has almost completely formed over the path of the bullet, although at the centre of the track there is a hollow region reaching all the way down to the bullets position.

Cross sectional images of the bullet’s track are shown in Figure 4.17. After 3 ps we see the bullet has started to penetrate the surface of the lattice and is sending shock waves into the material. The existence of these shockwaves can be observed in Figure 4.17(a), where we see the bottom half of the lattice retains its crystal structure, while the top half is effected by the shock waves. In Figures 4.17(b) and 4.17(c) we see these shock waves have propagated
4.3. RESULTS

(a) 0 ps
(b) 8 ps
(c) 20 ps
(d) 120 ps

Figure 4.16: Images of the surface during the 1,000 m/s bullet impact on 4H SiC.
Figure 4.17: Cross sectional images of the 1,000 m/s bullet on 4H SiC.
throughout the entire lattice. After 10 ps the bullet is further into the material. A large number of atoms are being pushed out of the lattice and some are sputtered. There is an amorphous region surrounding the bullet and there is some disturbance in the entire system. After 120 ps the bullet is at its target depth in the material. There is a clear track of damage in the path of the bullet. Away from this region the system appears to have largely retained its crystal structure although some disturbance is evident.

A cross section taken on the $x, z$ plane through the path of the bullet is shown in Figure 4.18. We see there is an amorphous core region around the path of the bullet, similar to that seen in the 6H simulation, although in this case the amorphous region is more square in shape, due to the different crystal structure. The diameter of this damaged region is approximately 10.9 nm, compared to the 8 nm diameter of the bullet. At the centre of this track region is a completely hollow section with a diameter of 1.3 nm. Ripples appear to occur from this track region to the edge of the lattice (the rings around the damaged region). This effect was also evident in the 1,000 m/s impact on 6H SiC.

Figure 4.19 shows the relative densities of the bullet region and the entire lattice against time. The graph has the same shape as in the 6H simulation, with a large drop as the bullet enters the lattice ($\approx 0.63$ times its original density). The density then increases as atoms
recoil back to the bullet region after the bullet has passed. The relative density of the bullet region stabilises at just over 75% its original density, very similar to the 6H case. This shows that density effects in the bullet track region do not seem to depend on crystal structure. The decrease in density of the entire system is due to atoms being ejected from the lattice, or thrown above the height of the original surface.

The temperatures of the bullet region and entire lattice against time are plotted in Figure 4.20. The initial sharp increase in temperature in the bullet region corresponds to the bullet impacting the surface and transferring a lot of kinetic energy to the atoms close
4.3. RESULTS

(a) 0.6 ps
(b) 3.2 ps
(c) 12 ps

Figure 4.21: Graphs showing the average temperature in the lattice as a function of distance from the bullet, for the 1,000 m/s on 4H simulation.

Figure 4.22: An image of the largest cluster (9 atoms) present after 120 ps of the 1,000 m/s bullet on 4H SiC.

to it. The temperature of this region peaks at approximately 3,800 K and then tails off as the bullet pushed further into the lattice. The temperature drops to around 1,500 K eventually. The graph has the same shape as in the 6H simulation. Figure 4.21 shows the average temperature in the lattice against distance from the centre of the bullet. Initially we see a sharp peak in the temperature at the edge of the bullet, with the peak reaching approximately 7,000 K after 3.2 ps. The wave of kinetic energy has started to spread to the edge of the system at this point. After 12 ps we see the wave has reached the edge of the lattice and the peak temperature has begun to fall. The initial wave of kinetic energy from the impact point was calculated to be travelling at approximately 5,556 m/s.

A lot less sputtering was observed than in the 6H simulation: only 155 atoms in this case. Of these, 62 were lone atoms and the rest formed clusters of 2 or more atoms. The maximum
cluster size was only 9 atoms and is shown in Figure 4.22. This cluster has a total kinetic energy of 3.3 eV (0.37 eV per atom) and a total potential of $-35.8$ eV ($-3.98$ eV per atom). The temperature of this cluster was calculated to be 990 K and it was travelling at a speed of 795 m/s.

Figure 4.23 shows images of slip systems that remain activated after 120 ps. The first image shows a dislocation has formed in the \{1 1 1\} direction from the path of the bullet. Figure 4.23(b), taken from underneath the lattice, shows the extent of the dislocation and also demonstrates the crystal structure of the material. Slip planes in the \{1 1 1\} direction are also commonly seen in FCC metals [142], potentially verifying the metal-like behaviour of SiC seen experimentally [131]. Thus the 4H system appears more susceptible to slip, since no slip planes were activated during the 6H simulation.

### 4.3.4 6H SiC at 100 m/s

A further bullet impact simulation was carried out on system A from Table 4.1, the 6H system. All parameters remained the same as in the original 6H simulation except for the bullet speed, which was reduced to 100 m/s to investigate speed effects. A time of 400 ps
was simulated.

Figure 4.24 shows images of displaced atoms during the simulation. The first image, taken after 6.5 ps, shows the bullet just making contact with the surface. We see a wave of displaced atoms spreading across the surface away from the bullet. After 20 ps, in Figure 4.24(b), we see a similar image to the 1,000 m/s 6H simulation with a large number of displaced atoms moving away from the point of impact, although not as many as during the 1,000 m/s impact on 6H SiC. After 100 ps the bullet has pushed further into the material causing a large number of atoms to be thrown up around it and onto the surface. However, due to the lower bullet speed and thus less energy being imparted to the substrate, most of these atoms do not have enough kinetic energy to escape.

Figure 4.25 shows cross sections of the lattice across the path of the bullet. We see the damaged track in the path of the bullet and material thrown onto the surface. There is distortion in the layers of atoms causing a ripple effect radially from the bullet. This occurs in close proximity to the bullet. A cross section showing the track of the bullet is shown in Figure 4.26. We see the same damaged region around the path of the bullet as in the other simulations. The diameter of this region is 11.3 nm compared to the diameter of the bullet of 8 nm. There appears to be some ripple effects in the rest of the system although the crystal structure appears to remain mostly intact.

The relative densities of the entire lattice and the bullet track region are plotted in Figure 4.27. As in the previous simulations we see the density of the bullet region drop significantly as the bullet penetrates the system, although at a slower rate in this case, due to the lower speed. The density reaches a minimum of roughly 68 % of its original density, after approximately 120 ps. The density increases before dropping again as the bullet moves slowly through the lattice.

Plotted in Figure 4.28 is the average temperature in the system as a function of distance from the centre of the bullet. In the first graph (Figure 4.28(a)) we see a large spike in temperature (2,000 K) as the bullet first hits the surface of the lattice. 2 ps later, in
Figure 4.24: Images showing displaced atoms at different points of the 100 m/s 6H simulation. Black coloured atoms are carbon, yellow silicon. The dimensions of the simulation cell are \(34.4 \times 34.4 \times 34.5\) nm\(^3\).
4.3. RESULTS

(a) 25 ps

(b) 400 ps

Figure 4.25: Cross sections showing the path of the bullet in the material, for the 100 m/s impact on 6H SiC.

Figure 4.26: Cross section viewed from the top of the path of the bullet in the material, showing the amorphous track of the bullet. The dimensions of the simulation cell are $34.4 \times 34.4 \times 34.5$ nm$^3$. 
Figure 4.27: Relative densities of the entire system and the bullet track region against time for the 100 m/s bullet on 6H SiC.

Figure 4.28: Graphs showing the average temperature in the lattice as a function of distance from the bullet, for the 100 m/s on 6H SiC simulation.
4.3. RESULTS

Figure 4.29: A graph showing the number of displaced atoms against time during the larger 1,000 m/s bullet on 6H SiC simulation.

Figure 4.28(b), the peak has dropped to approximately 500 K and a wave of kinetic energy has started to spread with the front of the wave approximately 16 nm from the centre of the bullet. This wave corresponds to the displacement of surface atoms we saw in Figure 4.24(a) and was calculated to be travelling at approximately 6,200 m/s.

Almost no sputtering was observed during this lower speed bullet simulation, with only 26 single atoms being ejected from the lattice during the entire simulation. As in the higher speed 6H simulation we did not see any activation of slip planes during this simulation.

4.3.5 6H SiC larger bullet at 1,000 m/s

A bullet impact was performed on the much larger 6H SiC system C from Table 4.1. The dimensions of the system in the $x$ and $z$ directions were double those of the smaller 6H system, with 4 times as many atoms (16.3 million). In this simulation the bullet was given a radius of 8 nm and initial speed of 1,000 m/s. The simulation was carried out for 123.2 ps.

The number of displaced atoms against time is plotted in Figure 4.29. The graph has the same shape has the smaller 6H simulation, with the number of displaced atoms rising initially, as the bullet first hits the surface, oscillating for a period and then starting to level off. However a larger proportion of atoms are displaced in this case: approximately 42 %.
Figure 4.30: Cross sectional images showing the path of the bullet, taken during the larger bullet on 6H simulation.
4.3. RESULTS

Figure 4.30 contains images of cross sections of the lattice, showing the path of the bullet in the material. After 3.6 ps the bullet has just started to push into the material, causing displacement to atoms nearby. An amorphous layer of atoms forms in close proximity to the bullet. After 10 ps, in Figure 4.30(b), the bullet is much further into the material. The amorphous layer around the bullet is still visible and we see a large number of atoms being thrown out of the lattice. This is seen experimentally, where during penetration a fine granular material is observed just in front of the projectile, and flows out around the projectile as it pushes further into the material [132, 143]. In Figure 4.30(c), taken after 40 ps, we see large clusters of atoms being ejected from the system, along with many single atoms and smaller clusters. Atoms thrown up onto the surface with insufficient energy to escape the lattice form a rim around the crater left in the wake of the bullet. Finally, after 123.2 ps (Figure 4.30(d)) the bullet has reached its target depth in the material. The system appears to largely retain its crystal structure away from the bullet. The diameter of the bullet track was calculated to be approximately 19.3 nm.

Images taken from above the surface of the lattice at different times during the simulation are shown in Figure 4.31. The first image, taken after 4 ps, shows the system just after the bullet has made contact. There is a wave of damage travelling across the surface, away from the bullet. Figure 4.31(b) shows the system 8 ps later. Here the bullet has pushed further into the substrate and a large number of atoms are being thrown up onto the surface and ejected from the lattice. By 40 ps (Figure 4.31(c)) the bullet has continue to push into the material causing a large number of atoms to be ejected from the system. Large clusters of atoms are observed being ejected from the lattice. After 120 ps we see most of the sputtered atoms have left the image. A lot of debris has been thrown up onto the surface around the bullet. In this simulation there has been no reconstruction (or filling) of the path of the bullet after it has passed into the material, as we saw in all the other simulations. This could perhaps be due to the top of the bullet not being as far into the material as in the other simulations (same target depth but larger radius), although it is more likely to be as
Figure 4.31: Images from above the surface of the lattice during the larger bullet on 6H SiC simulation. Atoms thrown up above the surface in (b) and (d) show indications of the hexagonal symmetry of the 6H structure.
4.3. RESULTS

Figure 4.32: Relative densities of the entire system and the bullet track region against time, for the bigger 6H system simulation.

a result of the much larger number of atoms being ejected from the system.

Figure 4.32 shows the densities in the bullet region and the entire lattice against time. Initially the density in the bullet region behaves in the same way as in the smaller 6H 1,000 m/s simulation, with the density dropping quickly followed by a slight recovery and then dropping further. However, where in the previous simulation the density then recovered slightly due to atoms filling the space behind the bullet, in this simulation the density hardly increases at all from its minimum (approximately 65% its original density). This is due to a lot more atoms being ejected from the lattice rather than filling the space behind the bullet. The drop in density of the entire lattice is due to atoms being ejected from the system or thrown up on top of the surface.

The temperatures of the bullet region and the entire lattice against time are plotted in Figure 4.33. The graph has the same shape as the smaller 6H, 1,000 m/s simulation. The temperature in the bullet region peaks soon after the bullet has impacted the surface, reaching a maximum temperature of 4,068 K after 9 ps. The temperature in this region then drops gradually and after 123.2 ps it is 880 K. By this point the average temperature of the entire lattice has risen to 408 K. Figure 4.34 shows plots of the temperature in the lattice as a function of distance from the centre of the bullet. After 1.6 ps we see a spike in temperature at the edge of the bullet reaching up to 4,000 K. In Figure 4.34(b), after 3.2 ps,
Figure 4.33: Average temperature in the entire system and the bullet track against time, during the larger 6H system simulation.

Figure 4.34: Graphs showing the average temperature in the lattice as a function of distance from the bullet during the larger 6H system simulation.
we see a wave of kinetic energy travelling through the system, away from the bullet. By 5.6 ps (Figure 4.34(c)) the wave has reached the edge of the surface. The wave was calculated to be travelling at a speed of 6,105 m/s.

During this simulation a large number of atoms were sputtered. After 123.2 ps a total of 109,055 atoms had been ejected from the lattice, consisting of 9,717 single atoms with the rest making up 16,413 clusters of 2 or more atoms (6 atoms per cluster on average). There were 44 clusters with 100 or more atoms. The largest observed cluster size was 426 atoms and is shown in Figure 4.35. This cluster is made up of 232 C and 194 Si atoms. It is travelling at a speed of 1,009 m/s, has a total kinetic energy of 289.4 eV (0.68 eV per atom) and has a total potential energy of $-1,978.2$ eV ($-4.6$ eV per atom). The kinetic energy can be broken down into the kinetic energy of the centre of mass (43.8 eV), the angular kinetic energy (161.3 eV) and the internal vibrational energy (84.3 eV). The temperature of the cluster was calculated to be 1,531 K (the melting point of SiC is approximately 3,000 K). A large number of C dimers are observed in the cluster in between Si atoms.

Figure 4.36 shows another large cluster observed at the end of the simulation. The cluster
Figure 4.36: Images of two large clusters present after 123.2 ps.

in Figure 4.36(a) contains 310 atoms (156 C and 154 Si). The total potential energy of the cluster is $-1,416$ eV or $-4.57$ eV per atom. The total kinetic energy of the cluster is $222$ eV (0.72 eV per atom) and can be broken down into the kinetic energy of the centre of mass (40.4 eV), the angular kinetic energy (117.9 eV) and the internal vibrational energy (63.6 eV). The temperature of the cluster was calculated to be 1,588 K and it was travelling at a speed of 1,117 m/s. The 247 atom cluster shown in Figure 4.36 consists of 143 C and 104 Si atoms. This cluster is travelling at a speed of 1,627 m/s. It has a total potential energy of $-1,186$ eV ($-4.8$ eV per atom) and a total kinetic energy of 216 eV (0.88 eV per atom). The kinetic energy of the centre of mass of the cluster is 64.1 eV and the angular kinetic energy is 96.2 eV, leaving an internal vibrational energy of 56.0 eV. From this the clusters temperature of 1,754 K was obtained. As noticed in the cluster shown in Figure 4.35 we observe that all the C atoms in both these clusters occur as dimers, in between Si atoms. Whereas the cluster shown in Figure 4.35 looks quite spread out both of these clusters appear more concentrated around their centres of mass.

Figure 4.37 shows slipped atoms at the end of the simulation. As in the other 6H simulations, and in contrast to the 4H simulation, no activation of slip planes was observed.
4.4 Conclusions

Using our model we have shown it is possible to model bullet impacts on SiC using large scale MD simulations. We have looked at impacts on two different structures of SiC, namely 4H and 6H. The differences in the crystal structures of the polytypes were made obvious by the shape of the structures that formed on the surface of the lattice; and also by the shape of displaced atoms in the material. Dislocations were observed to propagate in the $\{1 \ 1 \ 1\}$ direction in the 4H lattice following the impact, but none were observed in the 6H simulations.

In all simulations most of the damage in the system occurred in the bullet’s track or very close to the bullet. The damaged region just in front of the bullet is observed experimentally and is known as the “Mescall zone” [143] or the “failed zone” [132]. In agreement with experimental work we observed the material from this zone flow around the bullet and out of the lattice or onto the surface. In all the simulations using a bullet of diameter 8 nm the amorphous bullet track region was a similar size of approximately 11 nm. This shows that varying the speed of the bullet, and also the structure of the material, does not seem to effect the size of the damaged region left in the path of the bullet. However varying the size

Figure 4.37: Slipped atoms after the larger bullet impact on 6H simulation.
of the bullet does effect the size of this region, as we saw in the case of the 16 nm diameter bullet. In this case the diameter of the defective track was approximately 19.3 nm. In terms of the difference between SiC structures it was noticed that a larger percentage of atoms were displaced during the 6H 1,000 m/s bullet impact than for the same bullet impacting 4H SiC. It has been shown that the cohesive energy is greater in the 4H structure [141], which could explain this finding.

In the simulations we observed a wave of kinetic energy travelling through the system as a result of the bullet impact. Wave speed values were all calculated to be in the region of 6,000 m/s and did not depend on the polytype or the bullets speed or size.

A large difference in sputtering was observed in the different simulations. The 100 m/s impact resulted in hardly any sputtering. The 1,000 m/s impact on 4H SiC resulted in less sputtering than on the 6H system, with no large clusters forming in the 4H case. The total number of sputtered atoms in the 6H case was 2,846 atoms, whereas only 155 atoms were sputtered in the 4H simulation. The smaller bullet on 6H system resulted in the formation of a few large clusters, the largest being a cluster of 318 atoms. A much larger amount of sputtering was observed in the larger bullet on 6H simulation, with 44 clusters containing 100 or more atoms and a largest cluster size of 426 atoms. Regarding the structure of the observed clusters we noticed that C atoms tend to form dimers separated by Si atoms. The temperatures of the ejected clusters were typically high, i.e. above 1,500 K where the melting point of SiC is approximately 3,000 K. The clusters were also observed to be moving quickly, typically with speeds in excess of 1,000 m/s.

From these results it would appear the 4H material could be more resistant to bullet impact since less damage was observed in the 4H substrate (where damage is characterised by the number of displaced atoms, as already discussed). Also, in the case of the 4H simulation, a lot less debris (or sputtering) was observed than in the 6H simulation. However, in the 4H simulation dislocations were seen to propagate in the material: something that wasn’t observed in any of the 6H simulations.
Chapter 5

Multiple impacts on Gold

5.1 Introduction

Surface topographies change as a result of the interaction of energetic particles with the surface. A large amount of experimental, theoretical and computational work has been carried out on the development of surface topographies following ion bombardment [16, 26, 38, 144]. Low energy bombardment may result in thin film deposition and has a number of important technological applications, for example the manufacture of low emissivity coatings on glass, hard coatings on tool bits and even deposition of polymers. At higher energies ($\gtrsim 100$ eV) ion beams can be used to etch surfaces such as in the manufacture of semiconductor devices or in depth profiling in surface analysis.

Sputtering (see Figure 5.1) is the ejection of atoms from a target surface as a result of bombardment by energetic particles. The process of sputtering has been the focus of many investigations since it was first discovered by Grove in 1852 [1]. Sputtering can be characterised using the sputtering yield: the number of atoms removed from the surface per incident particle. Also of interest are distributions of sputtered particles, for example their angles of ejection and kinetic energies. For crystalline targets the angular ejection patterns depend on the crystal structure and are usually sharp [16]. Sigmund, in his theoretical model
of sputtering [24], calculated that the peak in the distribution of kinetic energies of ejected atoms should occur at approximately half the cohesive energy of the material.

Traditionally MD simulations of multiple particle impacts have been carried out by modelling the cascade formed by a single impact for a period of time depending on the energy of the incoming ion, typically of the order of 10’s of picoseconds. Following this stage the system is relaxed using a method such as the damped MD technique (see Section 2.1.8), before a further impact is simulated. While the relaxation stage should remove excess energy from the simulation before the next impact, the whole step occurs on such a small time scale that the dose rate of incoming ions is much faster than those seen experimentally. One effect this could have is to cause a build up of defects in the surface region, since the migration and recombination of defects will occur on a much longer time scale than that accessible to MD simulation.

In this chapter multiple gold on gold impacts are simulated, using the traditional MD approach. This work was done in preparation for the following chapter, in which a new and improved methodology is applied to the same problem. Experimentally it has been observed that bombardment of the \{3 11 1\} surface of FCC metals leads to a large number of observable surface features forming, including etch pits and pyramids [17, 18]. Due to the difficulty in creating a suitably sized periodic lattice with the \{3 11 1\} orientation we chose the \{3 11 0\} surface for bombardment, which should behave similarly. This is a high index plane close to \{0 1 0\}, which has a lower surface energy. One might expect that such
Table 5.1: The Au systems that were used in the multiple impact MD surface erosion simulations. The systems were constructed with a \{3 11 0\} oriented free surface.

<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>Lattice volume (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 67,650</td>
<td>$11.3 \times 10.0 \times 10.2$</td>
</tr>
<tr>
<td>B 72,940</td>
<td>$11.6 \times 9.3 \times 11.4$</td>
</tr>
<tr>
<td>C 238,454</td>
<td>$20.9 \times 9.3 \times 20.8$</td>
</tr>
</tbody>
</table>

5.2 Computational method

The systems that were used for modelling surface erosion by successive MD impacts are shown in Figure 5.1. The systems had periodic boundaries in the x and z directions while the bottom layer of atoms in the system were held fixed. The successive impacts were performed by placing a gold atom in a random position, a fixed distance above the free surface. Projectiles were given a kinetic energy of 5 keV. Impacts were carried out either normal to the surface in question or with an angle of incidence of 60°. For each impact the MD (ballistic) phase was carried out for 15 ps, after which damped MD was run for a further 5 ps to remove excess energy from the system before the subsequent impact. Initially the temperature of the system was 0 K and no thermostat was used during the simulations.

5.3 Results

5.3.1 Normal impacts, smaller system

100 successive Au atom impacts were simulated at normal incidence on system A from Table 5.1, equivalent to a dose of approximately $8.7 \times 10^{13}$ Au ions per cm$^2$.

Figure 5.2 shows snapshots of the surface after different numbers of impacts. Figure 5.2(a) shows the system after 20 impacts, equivalent to a dose of $1.7 \times 10^{13}$ ions per cm$^2$. Here we see the formation of craters in the surface with facetted edges. After a further 20 impacts
Figure 5.2: Images showing snapshots of the surface after different numbers of 5 keV normal impacts. Atoms are coloured by height with dark blue coloured atoms above the height of the original surface and red atoms at the depth of the deepest crater. Images (c) and (d) show the same surface from opposite sides of the lattice.
(Figure 5.2(b), viewing the lattice from the opposite direction) we see the topography has changed little, with the addition of some small craters. Figures 5.2(c) and 5.2(d) show the surface after 100 impacts from different perspectives. We see large, deep craters with faceted edges have formed. The sputtering yield for this simulation was calculated to be approximately 18.9 atoms per ion. The sputtering yield found experimentally for this bombardment energy is approximately 15 atoms per ion [16], which is lower than the value found here.

5.3.2 60 degrees impacts, smaller system

Impacts with an angle of incidence of 60° were carried out on system B from Table 5.1. A total of 65 successive impacts, equivalent to a dose of $5 \times 10^{13}$ ions per cm$^2$, were simulated.

Images of the surface taken throughout the simulation are shown in Figure 5.3. The topography resulting from one impact is shown in Figure 5.3(a), where we see a large crater has formed with material thrown up around the crater. After 40 impacts (Figure 5.3(b)) the topography has roughened, with the formation of a number of craters. Material has also been thrown up onto the surface, creating a “spire” in the top corner of the lattice. Figure 5.3(c) shows the surface after 65 impacts, viewing it from the opposite side to the first two images (the arrow indicates the direction of the incoming ion at 60°). A large crater has formed on the near side, as a combination of many smaller craters. The sputtering yield during this simulation was approximately 18.6 atoms per ion. This value is similar to that found for the normal impacts on the same system and is higher than the experimentally found value.

Figure 5.4 shows images of the first impact on the surface at different times. In Figure 5.4(a), taken at 0.8 ps, we see a number of single atoms have been sputtered and a damaged region has formed around the site of the impact. After 3 ps (Figure 5.4(b)) we observe the sputtering of dimers as well as single atoms. Also we can see the beginning of the formation of a crater in the surface, with a number of atoms thrown up above the surface around this crater. After 12 ps, in Figure 5.4(c), we see a number of clusters of atoms have
Figure 5.3: Snapshots of the surface after different numbers of impacts during the 60°, smaller system simulation. In (a) and (b) the ions are angled in from the nearside while in (c) the image is taken from the opposite side (the arrow indicates the direction of the incoming ions in this case).
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(a) 0.8 ps
(b) 3 ps
(c) 12 ps
(d) Post relaxation

Figure 5.4: Images showing the first impact during the 60° angle of incidence simulation. The colouring scheme is given in Figure 5.3(d). In (a), (b) and (c) the incoming particle is angled in from the nearside. In (d) the particle is angled in from the left to right.
also been sputtered from the system. The crater that has formed in the surface is shown in Figure 5.4(d): taken after the relaxation stage of the simulation from a different angle. We can see the crater that has formed is deep, with its base at approximately 7.6 nm (the surface is roughly 9.3 nm). The ion was angled into the surface from left to right as we look at it in this image. Atoms have been thrown up onto the surface all around the crater. This impact is an example of a high yield event with a total of 72 atoms sputtered, well above the average.

5.3.3 Normal impacts, larger system

Normal impacts were also simulated on system C from Table 5.1. This system has a much larger free surface area than the previous system as we are interested in seeing whether this change in area influences the topography development. 377 successive impacts were performed, equivalent to a dose of approximately $8.7 \times 10^{13}$ Au ions per cm$^2$ (the same as the smaller system).

Figure 5.5 shows images of the surface of the lattice during a single impact (the first impact). The first image shows the site of the impact (within the white lines) just after the particle has hit the surface. A small amount of damage is visible. 1 ps into the simulation (Figure 5.5(b)) and we see the damage has spread to a larger area although no crater is visible yet. 2 ps later we see, in Figure 5.5(c), a crater has started to form as more atoms are ejected from the system. Also visible is a rim forming around the crater (red atoms). After 15 ps we see the crater has grown. The bottom of the crater is at approximately 7.5 nm, a depth of roughly 1.8 nm from the surface. This impact is an example of a high yield event during which a total of 77 atoms were sputtered.

A low yield impact is shown in Figure 5.6. This is the second impact on the system, the crater from the first impact is still visible. The site of the current impact is outlined in Figure 5.6(a). We see a small amount of damage at the impact site due to the ion channelling into the lattice, rather than depositing its energy near the surface. After 1 ps we observe
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Figure 5.5: Images showing a single normal incidence, 5 keV impact, resulting in the formation of a large crater on the surface. The white circles in (a) shows the site of the impact (note the impact occurred on a periodic boundary. Atoms are coloured by height, the scale is shown in Figure 5.11(d).
Figure 5.6: Images showing a single normal incidence, 5 keV impact resulting in little surface damage or sputtering, due to channelling of the ion. The white circle in (a) shows the site of the impact and (d) shows the colouring scale.
some displacement around the site of the impact but no crater appears to be forming. After the simulation, in Figure 5.6(c), we can see a small crater has formed in the surface, much smaller than the one shown in Figure 5.5. A few atoms have been thrown up onto the surface around the impact site, but nowhere near as many as in the previous high yield event. The sputtering yield for this impact was only 6 atoms. We can see the difference between these first two impacts clearly in Figure 5.7, a contour plot of the surface following the second impact. Bearing in mind the height of the surface is roughly 9.3 nm we see that the first impact created a crater reaching down to a height of 7.6 nm and with a diameter of approximately 3 nm. The rim around the crater reaches a peak height of approximately 9.8 nm. In contrast, a crater has hardly formed following the second impact, reaching down only to a height of roughly 9 nm and with a much smaller diameter.

Figure 5.8 shows atoms that have been displaced from their original positions during the impact shown in Figure 5.6. Initially, after 0.2 ps, we see a small amount of displacement around the path of the projectile. After 1 ps the area of displaced atoms has grown. A few picoseconds later and we notice there are now less displaced atoms, as some atoms recoil back to their original positions. This process continues, and after 15 ps we are left with a core region of displaced atoms, close to the path of the particle.

The distribution of the number of atoms sputtered per single ion is shown in Figure 5.9,
Figure 5.8: Images showing the subsurface cascade during the impact shown in Figure 5.6 (normal impact, 5 keV). Atoms are shown if they have been displaced from their original position by more than 1.3 Å.
for 377 ions in total. The distribution has a log-normal shape with a few high yield events (up to 124 atoms per ion) in the tail. This is the shape expected when bombarding a perfect crystal [2]. The peak number occurs between 4 and 20 atoms per ion, with approximately 56 % of the impacts resulting in a yield in this range. No atoms are sputtered during just under 10 % of the impacts. The sputtering yield was calculated to be 17.6 atoms per ion. This is slightly lower than the value we obtained when simulating impacts on the smaller system, and closer to the experimental value of approximately 15 atoms per ion.

Figure 5.10 shows graphs of the average surface height and root mean square roughness against the number of impacts. Initially the average surface height increases slightly (by approximately 0.1 nm) due to atoms being thrown up onto the surface. However as the number of impacts increases more atoms are sputtered and craters merge together, the surface height starts to drop. The roughness increases immediately following the first impacts, as craters form and atoms are thrown onto the surface, and eventually starts to level off.

Snapshots of the surface topography are shown in Figure 5.11. After 120 impacts, equivalent to a dose of $2.8 \times 10^{13}$ ions per cm$^2$, the surface has developed a rough topography with a number of smaller craters dotted around the surface. At this stage of the simulation the craters are all formed by single impacts, i.e. no craters have merged to form larger ones. Figure 5.11(b) shows the topography after 260 impacts, a dose of $6 \times 10^{13}$ ions per cm$^2$. We
observe more craters in the surface which appears to have roughened. We also notice that, due to the higher dose, larger craters have formed as combinations of smaller ones created by single impacts. After 377 impacts, or a dose of $8.7 \times 10^{13}$ ions per cm$^2$, more larger craters are apparent in the topography. As the dose increases smaller craters are joined to make larger ones, reducing the overall height of the surface. This can also lead to a reduction in the surface roughness which, as a result of many small craters, became more rough. As the craters become larger there is less variation in surface height.

Plotted in Figure 5.12 are the total number of point defects in the system against the number of impacts. Over the first twenty impacts we see a linear increase in the number of defects in the system. The graph follows a similar trend to Figure 5.10(b), which shows the surface roughness, and indicates there a link between surface roughness and the number of defects in the system. At the end of the simulation (377 impacts) there were approximately 20,000 defects in the system (the linear increase did not continue). This is a large number of defects and could be a result of the methodology not allowing time for the defects to recover.
5.3. RESULTS

(a) 120 impacts \( (2.8 \times 10^{13} \text{ ions per cm}^2) \)

(b) 260 impacts \( (6 \times 10^{13} \text{ ions per cm}^2) \)

(c) 377 impacts \( (8.7 \times 10^{13} \text{ ions per cm}^2) \)

(d) Colour by height

Figure 5.11: Images showing the surface topography at different stages of the larger normal impacts simulation. Atoms are coloured by height as shown in (d).
5.3.4 60 degrees impacts, larger system

Impacts with an angle of incidence of 60° were also performed on system C from Table 5.1. A total of 400 successive impacts were simulated, equivalent to a dose of approximately $9.2 \times 10^{13}$ Au atoms per cm$^2$.

A typical impact event is shown in Figure 5.13. The arrow and circle in Figure 5.13(a) show the direction of the incoming ion (the angle of incidence is 60°) and its impact site. In Figure 5.13(b) we see the initial damage created by the impact which is spreading across the surface in the direction of the arrow in Figure 5.13(a). After 1.1 ps (Figure 5.13(c)) this wave has spread further away from the impact site, approaching the site of a previous impact. Also apparent is a small crater beginning to form. At the end of the simulation we see the wave of damage has retracted and damage is only visible in the region around the impact site, including a small crater on the surface. 18 atoms were sputtered during this impact.

Images showing atoms displaced from their original positions, corresponding to the impact shown in Figure 5.13, are shown in Figure 5.14. The arrow in Figure 5.14(a) indicated the direction of the incoming ion (at an angle of incidence of 60°). In contrast to the corresponding figure for the normal impacts (Figure 5.8), where the cascade evolved down into the lattice, the cascade in this case forms an elliptical shape due to the angle of incidence.
Figure 5.13: Images showing a typical impact event during the 60° impacts on larger surface. The white circle in (a) shows the impact site and the arrow shows the direction of the incoming ion (all images are orientated in the same way).
Figure 5.14: Images showing the subsurface cascade during the impact shown in Figure 5.13 (60° angle of incidence). Atoms are shown if they have been displaced from their original position. The arrow in (a) shows the direction of the incoming ion. The arrows in (c) show atoms ejected as a result of focused collisions from the ion track (not possible with normal incidence).
Initially the area of displaced atoms is small, around the impact site. After 0.5 ps the number of displaced atoms has grown significantly. At the end of the simulation we see the number of displaced atoms has decreased slightly but is still quite high. The arrows in Figure 5.14(c) indicate atoms that were sputtered as a result of focussed collisions from the ion track. This is not possible with normal incidence impacts.

Figure 5.15 shows the distribution of the number of atoms sputtered per single ion (400 impacts in total). The peak in the distribution occurs early, between 4 and 8 atoms per ion, and tails off quickly after this. There are some high yield events, as you would expect when bombarding a perfect crystal. The shape is similar to the normal impacts case (Figure 5.9) although the peak is more distinct and occurs slightly lower. There are also more zero yield events in the 60° impacts case which is due to the incoming ion being reflected. The sputtering yield per ion was calculated to be 17.9, slightly higher than the normal impacts on the same sized system. The value is also slightly lower than that obtained for the 60° impacts on the smaller system and is closer to the experimentally obtained value of about 15 atoms per ion.

The average height of the surface and its roughness are plotted in Figure 5.16. The graphs have the same shape as in the case of normal impacts (Figure 5.10). The average height of the surface initially increases as adatoms are thrown onto the surface. After approximately
120 impacts the surface height begins to decrease and continues to do so as more atoms are sputtered from the system. The surface roughness increases sharply as the initial impacts take place and continues to rise until it appears to start to plateau after approximately 350 impacts.

Figure 5.17 shows snapshots of the surface of the simulation after different numbers of impacts. After 200 impacts, a dose of $4.6 \times 10^{13}$ ions per cm$^2$, we see a rough topography has formed, with many small craters on the surface. Following a further 100 impacts and we see a similar topography but with some larger craters forming as an amalgamation of smaller ones. After 400 impacts, equivalent to a dose of $9.2 \times 10^{13}$ ions per cm$^2$, much larger craters have formed (green and blue atoms) with one running most of the length of the system. In this final image an etch pit is visible on the near side of the lattice.

The total number of point defects in the system is plotted against the number of impacts, in Figure 5.18. Over the first twenty impacts we see a linear increase in the number of defects, as we did in the case of normal impacts, although the number of defects is less when the angle of incidence is 60°. The linear increase does not continue and at the end of the simulation, following 400 impacts, the total number of defects is approximately 17,000. This is less than the number of defects at the end of the normal impacts simulation. As in the
5.3. RESULTS

(a) 200 impacts \( (4.6 \times 10^{13} \text{ ions per cm}^2) \)

(b) 300 impacts \( (6.9 \times 10^{13} \text{ ions per cm}^2) \)

(c) 400 impacts \( (9.2 \times 10^{13} \text{ ions per cm}^2) \)

Figure 5.17: Images showing the surface topography at different stages of the larger, 60° impacts simulation. Atoms are coloured by height. The incoming ions are angled in from the nearside.

Figure 5.18: The number of defects plotted against the number of impacts, for the 60° impacts on larger system.
case of the normal impacts, the graph has a similar shape to the one for surface roughness (Figure 5.16(b)).

5.4 Conclusions

During this chapter multiple particle impacts were simulated using a traditional MD model. This chapter is useful in that it provides a comparison for the new methodology of simulating surface erosion (or growth) that is presented in the following chapter. Impacts across two different sized surfaces were modelled, with separate simulations for normal impacts and impacts with an angle of incidence of 60°. The effect of system size (or more accurately, surface area) can be seen by comparing Figures 5.2 and 5.11, which show images of the final surfaces of the normal impact simulations on the different sized surfaces, for the same fluence \(8.7 \times 10^{13}\) particles per cm\(^2\). The dimensions of the larger surface are double those of the smaller surface. If you take a quarter of the larger surface and compare it to the smaller surface we see the topography is quite similar, suggesting that surface area of the periodic systems does not effect the topography development. However with the smaller systems the sputtering yields we calculated were slightly higher than with the larger systems, which could be an effect of the size of the surface. All sputtering yields we obtained were slightly higher than the experimentally calculated values.

The topographies that develop in the simulations exhibit the same characteristics. A pitted topography forms with a large number of smaller craters. As the dose increases these craters join together to form larger craters. Faceting was observed on some crater walls.

The total number of point defects in the system was determined for the larger surface area simulations. We showed that initially there is a linear increase in the number of defects with the number of impacts. At the end of both simulations a large number of defects were observed in the system: approximately 20,000 and 17,000 for normal impacts and 60° impacts respectively. This is a result of the extremely high dose rate due to the time scales
that are achievable by MD simulation. It is impossible to model the processes that occur in between impacts using MD. In the next chapter we will use a new methodology for modelling surface erosion by successive impacts, using a multi time scale model that will allow realistic experimental dose rates to be modelled.
Chapter 6

Surface erosion over realistic time scales

6.1 Introduction

Molecular dynamics (MD) computer simulations have been used to investigate sputtering since the early work of Harrison [38], but have only really modelled single atom impacts rather than dose effects. Therefore, while angular ejection patterns from crystals [40], Wehner spots [15] and ejected ion energy distributions can be accurately modelled, predicted sputtering yields have never generally been in very close agreement with those found experimentally. One cause is due to the damage inflicted on the crystal by successive ion impacts. This was shown to be the case in the previous chapter when multiple gold on gold impacts were simulated using MD, and showed the number of defects increasing rapidly with the number of impacts.

In this chapter we present results from simulations of atomistic surface erosion by sputtering, using a hybrid MD-KMC multi time scale method, discussed in the methodology chapter (Section 2.2). This technique enables us to model realistic simulation times compared to those seen experimentally. Initial results obtained from the work done in this
<table>
<thead>
<tr>
<th>Number of atoms</th>
<th>Surface Lattice volume (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 8,000</td>
<td>{0 1 0} 4.1 × 8.2 × 4.1</td>
</tr>
<tr>
<td>B 13,500</td>
<td>{0 1 0} 6.1 × 6.1 × 6.1</td>
</tr>
<tr>
<td>C 8,602</td>
<td>{3 11 0} 4.6 × 7.0 × 4.5</td>
</tr>
</tbody>
</table>

Table 6.1: The Au systems that were used in the multi time scale surface erosion simulations.

chapter have been published in [146].

## 6.2 Computational method

Results within this chapter were obtained using the multi time scale technique described in the methodology chapter (Section 2.2). A pure Au crystal substrate was used with the different system sizes shown in Table 6.1. Either Au or Ar atoms were chosen to impact the low index \{0 1 0\} or high index \{3 11 0\} crystal surfaces.

The kinetic energy of the bombarding ion was fixed at 500 eV: high enough for sputtering to occur but small enough that the full cascades could be contained in the surface normal, $y$, direction, and also so that the calculations could be done in a sensible time frame. A lower energy was chosen than in the previous chapter since it was unclear whether the smaller system was large enough to contain higher energy bombardments (the sputtering yield was not particularly close to experiment, for example). The ion was placed in a random position a fixed height above the lattice, far enough away that there was initially no interaction between the incoming ion and the substrate. All impacts were performed normal to the surface in question. Periodic boundaries were applied in the $x$ and $z$ directions while the bottom layers of the system were held fixed and the Berendsen thermostat used for the next three layers. Before each deposition the entire substrate was heated to a temperature of 350 K for a period of 250 fs. Following this, for a further 250 fs, the atoms in the thermal layer only were held at 350 K. During the deposition the temperature of the thermal layers was held at 350 K. This temperature was chosen for comparison with similar growth simulations [146]. Particle impacts were simulated for a MD time of 20 ps: enough for the system to
return to its original temperature as the excess kinetic energy dissipated.

Using the method described in Section 2.2, transition searches are carried out in parallel with a bombardment event. Typically 200+ transition searches would be attempted before the transition selection process. Whereas all atoms in the system were included in the MD part of the simulation, during transition searches only defects and their surroundings are selected, reducing the number of included atoms to in the region of 600 – 700. A flux of \(2.64 \times 10^{15} \text{ ions cm}^{-2} \text{ s}^{-1}\) was used to determine the rate (and therefore probability) of an impact event occurring. At 350 K this meant the deposition had roughly the same probability as a transition with a barrier energy of 0.79 eV. We block transition barriers greater than 1 eV since they are unlikely to be accessible within the relevant time scale for the deposition event and chosen temperature: the deposition is over 1,000 times more likely to occur than a transition with a 1 eV barrier (as determined using Equation 2.34).

6.3 Gold on gold results

6.3.1 \{0 1 0\} surface

In this simulation we start with a perfect Au crystal containing 8,000 atoms and with dimensions 4.1 nm \(\times\) 8.2 nm \(\times\) 4.1 nm (system A from Table 6.1). Single Au atoms were used to bombard the \{0 1 0\} surface of the crystal with an impact energy of 500 eV. Throughout the simulation the temperature of the thermal layers at the bottom of the substrate was maintained at 350 K. During the simulation 3,098 steps were completed, corresponding to 0.854 s of real time. During this time the substrate was bombarded by 431 Au atoms, equivalent to a dose of \(2.6 \times 10^{15}\) Au atoms/cm\(^2\).

The distribution of transition energy barriers for diffusion between impacts in the simulation is shown in Figure 6.1. The graph shows no barriers above 0.85 eV (another reason for the omission of any barriers above 1.0 eV). The distribution shows few barriers at very low energies (\(<\) 0.2 eV), although the peak number of barriers occurs between 0.2 and 0.25
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Figure 6.1: The transition energy barriers for diffusion between impacts after bombardment of Au \{0 1 0\} by 500 eV Au atoms.

The majority of the rest of the transition barriers fall between 0.4 and 0.65 eV with a mean transition barrier of 0.4 eV.

An example of a transition with a barrier energy of 0.23 eV is shown in Figure 6.2, where we see the rotation and translation of a subsurface trimer. This is a transition that occurs frequently as you can see from the peak in the distribution between 0.2 and 0.25 eV. Another subsurface transition that occurs is shown in Figure 6.3. A five atom interstitial loop rotates and translates with a transition barrier energy of 0.58 eV. These are examples of the diffusion of smaller subsurface interstitial loops through the lattice. Figures 6.4 shows an example of surface diffusion that occurs between impacts. We observe the concerted motion of three atoms moving along a trench in the surface, towards a lower level.

The value for the sputtering yield was calculated to be 3.2 ± 2.6 atoms per ion, which can be compared to the experimentally observed sputtering yield of about 3 atoms per incident ion [16]. 9 % of the incoming ions were reflected from the surface. Figure 6.5 shows the distribution of the number of atoms sputtered per impacting atom. We see that in just under 14 % of the impacts no atoms are sputtered. The most common number of atoms to be sputtered per ion is 2, which happens in 16.7 % of the cases. The distribution tails off after 5 atoms per ion. The maximum number of atoms sputtered per incoming ion was 18: this occurred only once. The distribution looks similar to those calculated for perfect crystal
Figure 6.2: An example transition with a barrier of 0.23 eV. A subsurface trimer (coloured red) rotates and translates from its original position in the system. The arrows indicate the same atom in each image. The surrounding atoms in the bulk lattice have been removed for clarity.

Figure 6.3: An example transition with a barrier of 0.58 eV. A subsurface, five atom interstitial loop (coloured red) rotates and translates from its original position. The arrows indicate the same atom in each image. The surrounding atoms in the bulk lattice have been removed for clarity.
Figure 6.4: An example transition with a barrier of 0.75 eV. Three surface atoms move together along a trench in the surface towards a lower level. The moving atoms are coloured purple (and indicated by the arrows) while other atoms are coloured by height using a similar colour scheme to the one shown in Figure 6.9(d).

Figure 6.5: The distribution of the number of atoms sputtered per single Au projectile, after bombardment of the \{0 1 0\} surface. A total of 431 ion impacts occurred.
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Figure 6.6: Graphs showing the distribution of kinetic energies of sputtered atoms for the Au on \{0 1 0\} surface simulation: (a) shows the full distribution; and (b) a subset of the distribution.

surfaces with its log-normal shape and high yield events in the tail [2].

Figure 6.6 shows the distribution of the kinetic energies of sputtered atoms. The full distribution is shown in Figure 6.6(a) and shows the majority of sputtered particles have low energies. The distribution tails off quickly although there are a few sputtered atoms with high energies (≈ 140 eV). The first part of the distribution, up to 17 eV, is shown in Figure 6.6(b). Here we see that the peak occurs between 1 and 2 eV. The cohesive energy of Au is approximately 3.8 eV and so this peak falls at roughly half the cohesive energy. This was predicted in the theoretical work by Sigmund for random materials using Boltzmann transport theory [24].

The distribution of the angles of ejection of sputtered atoms is shown in Figure 6.7, where 0° is normal to the surface. We see the the shape of the distribution is almost that of a normal distribution, with a mean angle of ejection of 46°. The shape of the distribution is linked to the crystal structure of the substrate. The single peak occurs due to channelling and blocking by surface atoms with sputtering most likely to occur in close packed crystallographic directions. This shows that dose effects appear to have little effect on the angular distribution of sputtered atoms. However the statistics were not sufficiently good to show well defined Wehner spot patterns.
Figure 6.7: The distribution of the angles of ejection of sputtered atoms after bombardment of the \{0 1 0\} surface system.

Figure 6.8: Graphs showing the average height and RMS roughness of the surface of the substrate in the Au on \{0 1 0\} surface simulation.
Figure 6.8 shows the average height of the surface, and its roughness, against time. From Figure 6.8(a) we see that the height of the surface decreases almost linearly as time advances. Initially the average surface height was 7.94 nm and after 0.854 s this has dropped to an average of 6.90 nm, an erosion rate of 1.2 nm/s. We see from Figure 6.8(b) that surface roughness initially rises, due to the first impacts, and subsequently oscillates between 0.15 and 0.3 nm. The maximum average surface height is actually attained during the second step of the simulation as atoms are thrown up onto the surface as a result of the initial impact.

Figure 6.9 shows snapshots of the surface at various times during the simulation. In Figure 6.9(a) we see two craters in the surface with facetted edges and the surface appears rough. 0.036 s later, in Figure 6.9(b) these craters are no longer well defined and the surface appears less rough. In Figure 6.9(c) a new crater has formed with facetted edges. This behaviour of surface roughening due to atom impacts, followed by a period of healing, during which the surface becomes less rough due to craters filling, continues throughout the simulation. It is also made apparent by noting the oscillations in surface roughness over time in Figure 6.8(b). Under the surface of the lattice we observe the formation of interstitial loops of up to 17 atoms. A 13 atom interstitial loop is shown in Figure 6.10(a), which formed following an ion impact. Large loops like this one are immobile. They do not diffuse through the system but are annihilated during subsequent ion impacts. After a further impact, in Figure 6.10(b), we see the 13 atom loop has disappeared and a new 6 atom interstitial loop has formed. One more impact later and we see this loop has also disappeared (Figure 6.10(c)). Further on in the simulation we observe the formation of a new 12 atom interstitial loop, and the process continues. While these larger loops are immobile, smaller loops, such as the 3 and 5 atom loops shown in Figures 6.3 and 6.4 are mobile and can diffuse through the lattice in the manner depicted in those figures.

An image of the topography at the end of the simulation is shown in Figure 6.11. We observe a rough topography has developed, with the formation of one deep crater (blue
(a) 0.719 s or $2.20 \times 10^{15}$ Au cm$^{-2}$

(b) 0.755 s or $2.28 \times 10^{15}$ Au cm$^{-2}$

(c) 0.846 s or $2.52 \times 10^{15}$ Au cm$^{-2}$

(d) Atoms coloured by height in y

Figure 6.9: The surface topography after various simulation times is shown in (a), (b) and (c). The colour scheme for the atoms is shown in (d).
6.3. GOLD ON GOLD RESULTS

(a) 0.085 s or $2.74 \times 10^{14}$ \text{Au cm}^{-2}

(b) 0.093 s or $2.8 \times 10^{14}$ \text{Au cm}^{-2}

(c) 0.094 s or $2.86 \times 10^{14}$ \text{Au cm}^{-2}

(d) 0.209 s or $6.19 \times 10^{14}$ \text{Au cm}^{-2}

Figure 6.10: Subsurface interstitials and adatoms above the height of the original surface, during the Au on \{0 1 0\} simulation.
Figure 6.11: Images showing the surface at the end of the Au on \{0 1 0\} surface simulation.

Figure 6.12: The transition energy barriers for diffusion between impacts after bombardment of Au \{3 11 0\} by 500 eV Au atoms.

atoms) and a valley (green atoms) between a ridge (red atoms).

6.3.2 \{3 11 0\} surface

This simulation uses system C from Table 6.1. We bombard the \{3 11 0\} surface of the substrate with 500 eV Au atoms. The simulation was carried out for 2,696 KMC steps which resulted in a simulated time of 0.847 seconds. During this time 476 Au atoms bombarded the surface, a dose of $2.3 \times 10^{15}$ Au atoms/cm$^2$.

In Figure 6.12 the distribution of transition barrier energies is plotted. We see that the distribution is similar to the Au bombardment of the \{0 1 0\} surface, with a small number
6.3. GOLD ON GOLD RESULTS

Figure 6.13: An example transition with a barrier of 0.72 eV. A trimer of surface atoms move down a layer on a facet on the surface. The moving atoms are coloured purple, the rest of the atoms are coloured by height using a colour scheme similar to the one in Figure 6.9(d). This is an example of one the mechanisms by which the surface heals (becomes less rough).

of very low barriers and a large peak between 0.2 and 0.25 eV (over 30% of the barriers fall in this range). The average transition barrier was 0.36 eV and the distribution tails off well before the 1 eV cutoff that was imposed during the transition search.

Figure 6.13 shows an example of a surface diffusion event that occurred between impacts in the simulation. A trimer of surface atoms, located on a faceted edge, moves down the edge towards the bottom of the crater. This is an example of the mechanisms by which the surface heals: atoms that are thrown up onto the surface by impacts eventually diffuse into
Figure 6.14: The distribution of the number of atoms sputtered per single Au projectile, after bombardment of the \{3 11 0\} surface. A total of 476 impacts occurred.

the craters formed by the impacts, thus reducing the roughness of the surface.

Plotted in Figure 6.14 is the distribution of the number of atoms sputtered per single impacting ion. We see the distribution has a similar log-normal shape to the Au bombarding the \{0 1 0\} surface case, although the peak occurs at a lower value of 1 atom per single ion (17 % of the time). Roughly 12 % of the time no atoms are sputtered and we see a few high yield events occurring, with up to 13 atoms per ion being sputtered. The sputtering yield was calculated to be $3.4 \pm 2.6$ atoms per ion and 8.4 % of the time the incoming ion was reflected from the surface.

Figure 6.15 shows the distribution of the energy of atoms ejected from the lattice. The full distribution shows a peak at very low energies, that tails off quickly. Again there are a few sputtered atoms with very high energy ($\approx 120$ eV). The partial distribution shows there is a slight peak between 1 and 2 eV, as we saw with the \{0 1 0\} surface simulation, again in agreement with Sigmund’s model.

The mean angle of ejection of sputtered atoms was 46.3°. The distribution of the angles is shown in Figure 6.16. As expected the distribution is different to the \{0 1 0\} case as a result of the different surface orientation.

The average height of the surface is plotted against time in Figure 6.17(a), while the root mean square surface roughness is shown in Figure 6.17(b). We see that the surface initially
6.3. GOLD ON GOLD RESULTS

Figure 6.15: Graphs showing the distribution of kinetic energies of sputtered atoms for the Au on \{3 11 0\} surface simulation: (a) shows the full distribution; and (b) a subset of the distribution.

Figure 6.16: The distribution of the angles of ejection of sputtered atoms after Au bombardment of the \{3 11 0\} surface system.
has an average height of approximately 6.9 nm and after 0.847 s it has dropped to 5.95 nm, an erosion rate of 1.12 nm/s. The erosion rate appears to be almost constant as we see strong linear correlation on the graph. We see the surface roughness initially rise and then oscillate between approximately 0.15 and 0.3 nm, although it rises as high as 0.35 nm later in the simulation. These oscillations, which also appeared in the \{0 1 0\} surface simulation, are indicative of the erosion process. The surface roughens as atoms bombard it and then, due to surface diffusion, we see the surface roughness decrease with an overall drop in average surface height.

Figure 6.18 shows the final topography. The main features are a large ridge down the centre of the system and a deep crater in the lower left corner. The slopes of the ridge exhibit faceting, as do the walls of the crater.

### 6.3.3 Larger \{0 1 0\} surface

A simulation was run on a substrate with a larger \{0 1 0\} surface (system B from Table 6.1).

This surface across which the 500 eV Au atoms will impact has a surface area of 37.2 nm$^2$, compared to the simulation on system A that had a surface area of 16.8 nm$^2$. The larger
system was chosen to investigate surface size effects on the development of the topography using our new methodology. Due to the larger system size fewer impacts will be possible in a reasonable time. 1,509 simulation steps were carried out: a simulation time of 0.121 s. During this time 134 Au atoms bombarded the surface, a dose of $3.6 \times 10^{14}$ Au atoms/cm$^2$.

Plotted in Figure 6.19 is the distribution of transition energy barriers for diffusion between impacts. The average barrier was 0.43 eV. The distribution has the same shape as the smaller surface simulation in that there are few very low energy barriers and an initial peak occurring between 0.2 and 0.25 eV. In this case the peak number of barriers occurs between 0.4 and 0.45 eV.

Figure 6.20 shows an example of a transition that occur in the range 0.2 to 0.25 eV. This peak occurs in all the Au on Au simulations. We observe an atom on the surface, above a crater, move down the side of the crater to its base. In this way the surface heals between particle impacts (i.e. it becomes less rough). The energy barrier for this transition is relatively low at 0.20 eV, meaning this event occurs with high frequency. A graph showing the energies at the NEB images along the MEP for this transition is shown in Figure 6.21. It shows the new position for the atom is much more energetically favourable than the old one.
Figure 6.19: The transition energy barriers for diffusion between impacts after bombardment of the larger Au \{0 1 0\} surface by 500 eV Au atoms.

Figure 6.20: An example transition with a barrier of 0.20 eV. An atom (indicated by the arrow in (a) and coloured purple in (b) and (c)) diffuses down the edge of a crater. Other atoms are coloured by which layer they are in. This is one mechanism by which the surface heals (i.e. its roughness reduces).
Figure 6.21: Showing the relative energies at the NEB images for the transition shown in Figure 6.20. The forward barrier of 0.2 eV is much lower than the reverse barrier of approximately 1.1 eV.

An example of a transition with a barrier of 0.43 eV is shown in Figure 6.22. Two atoms on the surface, above a crater, move together to fill the crater. Initially the atom closest to the crater starts to move to fill the crater, and is followed by the second atom which moves to the space vacated by the first. This is another example of a how the surface “heals” between impacts (i.e. becomes less rough).

Figure 6.23 shows the distribution of the number of atoms sputtered per single impacting ion. The distribution has a similar log-normal shape to the previous simulations, peaking early at 0 to 1 atoms per ion, and tailing off by 12 atoms per ion. The sputtering yield was calculated to be $2.8 \pm 2.6$ atoms per ion, while a low proportion of incoming ions were reflected from the surface (9 %).

The distribution of the kinetic energies of sputtered atoms is shown in Figure 6.24. We see a similar shaped distribution to the other gold on gold simulations, with a peak at low energies that quickly tails off and a few high energy sputtered atoms. The distribution also shows the peak occurs at roughly half the cohesive energy of the substrate ($\approx 3.8$ eV in Au), as was predicted by Sigmund’s theory.

Figure 6.25 shows the distribution of the angles of ejection of sputtered atoms. The average angle of ejection was 46.9°. We see a peak at the centre of the distribution between 35 and 50°. This peak is a result of the crystal structure and is the same as expected when
Figure 6.22: An example transition with a barrier of 0.43 eV. Two atoms (coloured purple and indicated by the arrow in (a)) on the surface move together to fill a crater. The lower atom of the two fills the crater while the second moves into the space vacated by the first atom. All other atoms are coloured by height using a scale similar to the one shown in Figure 6.9(d).
Figure 6.23: The distribution of the number of atoms sputtered per single Au projectile, after bombardment of the larger \{0 1 0\} surface system. 134 impacts occurred in total.

Figure 6.24: Graphs showing the distribution of kinetic energies of sputtered atoms for the Au on larger \{0 1 0\} surface simulation: (a) shows the full distribution; and (b) a subset of the distribution.
bombarding a perfect surface.

Figure 6.26 shows both the average height of the surface and the surface roughness against time. The initial height of the surface was 5.9 nm and the final height was 5.8 nm, an erosion rate of 0.83 nm/s. The erosion rate is slightly lower due to the larger surface area. The graph shows an overall linear trend although it does oscillate a bit. The surface roughness increases initially before levelling off and increasing some more. We still see the oscillations in the roughness, a characteristic of the erosion process.

The final topography is shown in Figure 6.27. We observe the beginning of the formation of a rough topography, with some deeper craters forming with faceted edges. Whereas with the smaller system we saw the formation of a few main features (a ridge and one deep crater), the larger system allows for the formation of more features.

6.4 Argon on gold results

6.4.1 \{0 1 0\} surface

In this simulation 500 eV Ar atoms bombard the \{0 1 0\} surface of a perfect Au crystal (system B from Table 6.1). 2,098 steps were performed and a real time of 0.297 s was
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(a) Average height

(b) Roughness

Figure 6.26: Graphs showing the average height and RMS roughness of the surface of the substrate in the Au on the larger \{0 1 0\} surface simulation.

Figure 6.27: Images showing the surface at the end of the Au on larger \{0 1 0\} surface simulation.
simulated. During this time 132 Ar atoms bombarded the substrate, a dose of $7.9 \times 10^{14}$ Ar atoms/cm$^2$.

Figure 6.28 shows the distribution of transition barrier energies for diffusion between impacts. The distribution differs from the Au bombardment case (Figure 6.1) in that there are a much larger number of low energy ($< 0.1$ eV) barriers in the case of Ar bombardment. In fact over 45% of the barriers were under 0.1 eV, with an average transition barrier of 0.2 eV. These low energy barriers correspond to subsurface diffusion of implanted Ar atoms and result in the simulation time advancing more slowly than in the case of Au bombardment. The Ar diffusion is fastest when the Ar is clustered rather than isolated. When the Ar atoms cluster in voids formed in the lattice they can move around within the void with very low energy barriers (shown later). The implanted Ar does not accumulate into large bubbles at these energies, although small numbers can accumulate in voids (clusters of vacancies). Generally the Ar atoms diffuse to the surface or are exposed as the surface erodes. On average $6.3 \pm 2.3$ Ar atoms remain in the system at any one time, corresponding to $3.7 \times 10^{13}$ per cm$^2$.

The distribution of atoms ejected per single impact is shown in Figure 6.29. As in the case of Au bombardment the distribution has a log-normal shape with a few high yield events in the tail, corresponding to results calculated for perfect crystal surfaces. The most likely
number of atoms to be sputtered per impact is 3, occurring 18% of the time. The sputtering yield per impact was calculated to be $3.4 \pm 2.7$ atoms per ion, compared to an experimentally observed yield of about 3 atoms per ion [16]. A large proportion of the incident ions are reflected from the surface directly after impact (80%).

Figure 6.30 shows the distribution of kinetic energies of sputtered atoms. The distribution has a similar shape to the gold on gold simulations, peaking at low energies and tailing off quickly with a few high energy sputtered atoms. The partial distribution shows that the peak sputtered energy occurs between 0 and 1 eV, not 1 and 2 eV as was the case in the gold on gold simulations, and as was predicted by Sigmund’s model.

The average angle of ejection for the sputtered atoms was 43.8° with the distribution plotted in Figure 6.31. The distribution is similar to the gold on gold \{0 1 0\} simulations with a peak in the centre that tails off at both sides.

Figure 6.32 shows graphs of the average height of the surface and the surface roughness, against time. We see, once again, that the average height of the surface decreases almost linearly as time progresses. The initial height of the surface was 7.94 nm, which has dropped to 7.5 nm after 0.297 s, and erosion rate of 1.5 nm/s. The surface roughness increases initially and then oscillates between roughly 0.2 and 0.3 nm for the first 0.2 seconds of the simulation.
Figure 6.30: Graphs showing the distribution of kinetic energies of sputtered atoms for the Ar on \{0 1 0\} surface simulation: (a) shows the full distribution; and (b) a subset of the distribution.

Figure 6.31: The distribution of the angles of ejection of sputtered atoms, after bombardment of the \{0 1 0\} surface by Ar atoms.
After this the roughness appears to increase, and now oscillates between approximately 0.25 and 0.35 nm.

As the simulation progresses, adatoms are thrown up onto the surface, particles are ejected and a rough topography forms which eventually recovers. A remarkable feature of the process is the amount of self-healing that occurs between ion impacts. Adatoms thrown up onto the surface attain crystalline form, such as an incomplete deposited layer in growth simulations (see [147]). Interstitial loops with up to 15 atoms were observed to form below the surface but eventually decay during subsequent bombardments. Smaller loops of up to 5 atoms are mobile and can diffuse through the system. Snapshots of the topography after various simulation times are shown in Figure 6.33 and show the development of a facetted crater which forms after 0.01 s (the blue atoms in Figure 6.33(c)). Due to the continual ejection from and diffusion of atoms in the substrate, the crater no longer exists by 0.137 s as shown in Figure 6.33(d).

Corresponding images of the surface atoms that lie above the height of the original surface and subsurface interstitial loops and implanted Ar are shown in Figure 6.34. Figure 6.34(a) shows a subsurface interstitial loop of 8 atoms, together with a 4 atom Ar cluster and an isolated Ar interstitial near the surface. In Figure 6.34(b), 2 ms later following a further
Figure 6.33: The surface topography after various simulation times. Red spheres represent adatoms above the height of the original surface (≈ 8.1 nm), green and blue atoms lie below the height of the original surface (blue atoms at approximately 6.8 nm).
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(a) 0.085 s or $2.38 \times 10^{14}$ Ar cm$^{-2}$

(b) 0.087 s or $2.56 \times 10^{14}$ Ar cm$^{-2}$

(c) 0.090 s or $2.74 \times 10^{14}$ Ar cm$^{-2}$

(d) 0.137 s or $3.69 \times 10^{14}$ Ar cm$^{-2}$

Figure 6.34: Subsurface interstitials and adatoms above the height of the original surface, corresponding to the images shown in Figure 6.33. The arrow in (a) indicates a lone Ar atom near the surface which has escaped from the lattice by the time the later images are taken.
impact, the isolated Ar interstitial has diffused to the surface, the interstitial loop has decayed and a new 3 atom interstitial cluster has formed. Three of the clustered Ar atoms have begun to diffuse away from the fourth Ar atom. Following a further impact this cluster has totally disappeared (Figure 6.34(c)). Finally, in Figure 6.34(d), a new subsurface 8 atom interstitial loop has formed and 2 further Ar atoms have been ejected. Thus the erosion process continues with interstitial loops and craters continually forming and decaying as further Ar atoms impact the surface. This corresponds to the oscillations in the surface roughness noted in Figure 6.32(b): the surface becomes more rough after the formation of craters due to impacts, with the roughness subsequently reducing as the surface heals. The large interstitial loops formed as a result of particle impacts do not diffuse through the lattice, but decay as a result of further particle impacts on the surface.

Figure 6.35 shows an image and contour plot of the surface after 0.297 s (or $7.9 \times 10^{14}$ Ar cm$^{-2}$). The surface is in a rough phase and from the contour plot we can clearly see the presence of a hill and a valley. The images of the surface shows the facetted edges of the hillock. At this point the surface is very rough: Figure 6.32(b) shows at this point the roughness is over 0.35 nm and is at its peak roughness during the simulation. The peak
height of the hillock, at this point, is 8.4 nm, while the minimum point in the valley/crater has a height of 6.6 nm.

### 6.4.2 \{3 11 0\} Surface

This simulation was carried out on system C from Table 6.1. A total time of 1.218 s was simulated (2,168 steps), during which time 730 Ar atoms bombarded the \{3 11 0\} surface of the substrate. This corresponds to a dose of $3.5 \times 10^{15}$ Ar atoms/cm$^2$.

Figure 6.36 shows the distribution of transition energy barriers for diffusion between impacts. The average barrier was 0.28 eV. The distribution has a very similar shape to the Ar on Au \{0 1 0\} surface in the previous section. The peak number of barriers occur in the range 0 to 0.5 eV and correspond to the subsurface diffusion of implanted Ar atoms. The distribution tails off by 0.8 eV, well below the 1 eV cutoff we applied during transition searches (for speed purposes).

An example of one of the very low energy transitions that occur in the Ar on Au simulations is shown in Figure 6.37. Here we see a subsurface Ar atom move towards the surface in two stages: the Ar atom moves through a cluster of three vacancies formed due to sputtering. The small voids form in regions near to the surface, since most of the sputtered particles
Figure 6.37: An example transition with a barrier of 0.007 eV. An Ar atom (coloured purple) moves towards the surface of the system. The lattice has been cropped to show the path of the atom, with surrounding atoms coloured by height. We see the Ar atom move up through a cluster of vacancies.

Transitions with these very low energy barriers occur frequently (their probability is high) and result in very small advances in simulation time.

Figure 6.38 shows a transition with an energy barrier of 0.014 eV. This transition involves three implanted Ar atoms diffusing through a void in the lattice together. They will eventually diffuse towards the surface, as shown in the previous paragraph, and will either diffuse out of the system or be ejected during an impact. Subsurface Ar diffusion occurs very frequently and is one of the reasons the Ar ion simulations progress at a slower rate than the Au bombardment simulations. Small numbers of Ar atoms were observed to cluster in voids, such as the one shown in the image, which are formed due to sputtering as a result of the particle bombardment. Once in the voids the Ar atoms remain there until they are exposed to the surface by subsequent bombardments, or displaced by ballistic impact.

The calculated value for the sputtering yield was $3.5 \pm 3.1$ atoms per impacting ion. A large proportion (75%) of incoming Ar atoms were reflected from the surface, although this
Figure 6.38: An example transition with a barrier of 0.014 eV. Three subsurface Ar atoms (purple) diffuse through a void in the lattice formed by sputtering due to the ion impacts. All other atoms are coloured by height. The lattice has been cropped to the edge of the void for clarity.

Figure 6.39: The distribution of the number of atoms sputtered per single Ar projectile, after bombardment of the \{3 11 0\} surface. The surface was bombarded by a total of 736 Ar projectiles.
Figure 6.40: Graphs showing the distribution of kinetic energies of sputtered atoms for the Ar on \{3\,1\,1\,0\} surface simulation: (a) shows the full distribution; and (b) a subset of the distribution.

value is slightly lower than the \{0\,1\,0\} surface Ar impacts. The distribution of the number of atoms sputtered per incoming particle is shown in Figure 6.39. As in the other simulations we see the distribution has a log-normal shape, peaking at 1-2 atoms per impacting ion, with a few high yield events in the tail (a maximum of 20 atoms per ion were sputtered).

Figure 6.40 shows the distribution of kinetic energies of sputtered atoms. The graph has a similar shape to the other simulations, peaking at low energies with a few high energy sputtered atoms. The partial distribution shows the peak energy of sputtered atoms lies between 0 and 1 eV, as we found for the Ar on Au \{0\,1\,0\} simulation.

The angular distribution of sputtered atoms is plotted in Figure 6.41. As with the Au on Au \{3\,1\,1\,0\} simulation there is a broad peak due to the orientation of the surface. The average angle of ejection is $43.3^\circ$.

Figure 6.42(a) shows the average height of the surface against time, while the root mean square surface roughness is plotted in Figure 6.42(b). The initial height of the surface was 6.9 nm and the final height, after 1.218 s, was 4.78 nm. This is an erosion rate of 1.74 nm/s. The surface height appears to drop linearly as time progresses. The surface roughness increases initially, then oscillates between approximately 0.2 and 0.4 nm, before increasing towards the end of the simulation up to around 0.5 nm.
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Figure 6.41: The distribution of the angles of ejection of sputtered atoms, for the Ar on \{3 11 0\} surface simulation.

Figure 6.42: Graphs showing the average height and RMS roughness of the surface of the substrate in the Ar on \{3 11 0\} surface simulation.
An image of the final surface topography is shown in Figure 6.43. We see the formation of one large hillock (identified by the red atoms) and two deeper craters. It is possible that these craters will join following further bombardment, creating a larger crater as observed in the Ar on \{0 1 0\} simulation (Figure 6.35).

6.4.3 Larger \{0 1 0\} surface

This simulation was carried out on system B from Table 6.1, a substrate with a larger surface area than the previous Ar on \{0 1 0\} surface simulation: 37.2 nm$^2$ compared to 16.8 nm$^2$. The larger system was chosen to investigate the effects of surface size on the topography development. Due to the larger system size fewer impacts will be possible in a reasonable time. A total of 1,017 steps were carried out and a time of 0.083 s was simulated. 85 Ar atoms bombarded the surface in this time, a dose of $2.3 \times 10^{14}$ Ar atoms/cm$^2$.

The distribution of transition barrier energies is shown in Figure 6.44. The average transition barrier was 0.33 eV. As with the other Ar bombardment simulations we saw a large peak in the distribution for very low (< 0.1 eV) barriers, corresponding to the diffusion of implanted Ar atoms below the surface. This is then followed by a dip and another peak...
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Figure 6.44: The transition energy barriers for diffusion between impacts after bombardment of a larger Au \( \{0 1 0\} \) surface by 500 eV Ar atoms.

Figure 6.45: The distribution of the number of atoms sputtered per single Ar projectile, after bombardment of the larger \( \{0 1 0\} \) surface. Only 85 Ar atoms bombarded the surface during the simulation.

at around 0.4 to 0.5 eV.

The sputtering yield per single impact was calculated to be 3.6 ± 3.4 atoms per ion in this case, while 75 % of the incoming Ar atoms were reflected from the surface. Figure 6.45 shows the distribution of the number of atoms sputtered per single impact. Once again the distribution has a log-normal shape with some high yield events in the tail (up to 17 atoms sputtered per impact). The peak number of atoms sputtered per particle is 1, which happens in approximately 20 % of the cases.

Figure 6.46 shows the distribution of the energies of sputtered atoms and is a similar
Figure 6.46: Graphs showing the distribution of kinetic energies of sputtered atoms for the Ar on larger \{0 1 0\} surface simulation: (a) shows the full distribution; and (b) a subset of the distribution.

shape to the other simulations: peaking at low energies and with a few high energy atoms in the tail (up to \(\approx 130\) eV). The partial distribution shows the same thing we saw with the other Ar on Au simulations: the peak energy occurs between 0 and 1 eV. This differs from the Au on Au simulations, which peaked between 1 and 2 eV, and also from the peak predicted by Sigmund’s theory, i.e. the peak is bombardment species specific. In the case of Ar bombardment, as opposed to Au bombardment, the energy transfer is less as a result of Ar being lighter.

The average angle of ejection of sputtered atoms from the system was 44.5°. The distribution of the angles of ejection is plotted in Figure 6.47 and shows a peak near the centre of the distribution which tails off towards 0 and 90°. This is an effect of the crystal structure of the substrate and shows that the substrate heals under high dosage.

Figure 6.48 shows graphs of the average height of the surface and root mean square roughness, against time. The initial height of the surface is 5.9 nm and at the end of the simulation, after 0.083 s, the height has dropped to 5.8 nm, a surface erosion rate of 1.2 nm/s. The graph of the height against time has some linear correlation. The roughness of the surface increases, levels off at around 0.23 nm and then increases towards the end of the simulation. No oscillations are observed but it should be noted that this simulation has not
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Figure 6.47: The angular distribution of the distribution of the angle of ejection of sputtered atoms, for the Ar on larger \{0 1 0\} surface (6.1 $\times$ 6.1 nm$^2$) simulation.

Figure 6.48: Graphs showing the average height and RMS roughness of the surface of the substrate in the Ar on the larger \{0 1 0\} surface simulation.
run as far as the others and the oscillations may occur over a longer time scale.

An image of the surface at the end of the simulation is shown in Figure 6.49. We see similar features forming on the surface as in the case of the smaller system (see Figure 6.33). Etch pits are visible (blue atoms) with a large one forming in the bottom right corner of the surface. Red atoms indicate atoms thrown up above the height of the original surface. However some of the features look bigger in this case, which suggests further work is required to determine the effect of surface size on topography development.

## 6.5 Conclusions

We have shown that it is possible to model surface erosion over experimentally realistic time scales, using our multi time scale dynamics technique. This means we have been able to investigate dose effects on sputtering that have previously not been accessible to atomistic computer simulation.

In each of our simulations we observed the same erosion process. As the simulation progresses atoms are thrown up onto the surface and craters form as a result of particle bombardment. A rough topography forms which eventually stabilises – diffusion between impacts allows for partial healing of the surface, with craters filling before more are created.
6.5. CONCLUSIONS

The process continues, resulting in a steady drop in overall surface height, shown to be an almost linear decrease with time. This is obvious from the surface height and roughness graphs for each of the simulation, with the roughness oscillating as the surface becomes rough and then heals. Subsurface defects also exhibit the same healing process. Interstitial loops are formed as a result of bombardment events. Smaller loops, of up to 5 atoms, can diffuse through the system, while larger loops are immobile and persist until annihilated by subsequent particle impacts.

This crystal healing process explains why the angular ejection patterns of sputtered material from a crystal show such sharp features. The prediction by Harrison and Garrison from single impact MD simulations on perfect crystal surfaces [38, 40] that channelling and blocking by surface atoms is responsible for the patterns, also holds for higher experimental doses since the basic surface structure remains intact. The distributions of sputtered atoms also take the form you would expect when bombarding a perfect crystal (see [2]), with sharp features owing to the preferential sputtering along the close packed crystallographic directions. The sputtering yields were also seen to be in fairly close agreement with those seen experimentally [16] (≈ 3 atoms per ion for both Ar and Au ions). For the same sized systems, impacts on the \{3 1 1 0\} surface produced a slightly higher sputtering yield than those on the \{0 1 0\} surface. The numbers are too close to draw any real conclusions but a possible explanation could be more channeling is observed in the case of the lower index surface.

We saw the distributions of kinetic energies of ejected atoms took a similar shape to that expected from theoretical work. In the case of the Au on Au simulations the peak of the distribution occurred between 1 and 2 eV, roughly half the cohesive energy of Au (≈ 3.8 eV). This was predicted by Sigmund’s theoretical model of sputtering [24]. However this was not the case during the Ar bombardment simulations. In these cases the peak occurred lower, between 0 and 1 eV, suggesting it is bombardment species dependent. This is due to the large difference in weight between Ar and Au, which results in the Ar ion not transferring
as much energy during individual collisions.

Facets were observed to form on the sides of craters and ridges in the \{311\} surface simulations. This is particularly visible in the Au on \{311\} simulation. In the \{010\} surface simulations some faceting was observed on material thrown up onto the surface.

The main difference observed between the different bombardment species was that in the case of Ar we had a high number of very small transition energy barriers. These corresponded to the subsurface diffusion of implanted Ar atoms. In the examples shown we observed the diffusion of small clusters of Ar around voids in the lattice created by ion bombardments. These implanted Ar atoms remain in the system until they are exposed by the eroding surface or they diffuse out of the system.

Although the statistics generated for the larger systems were poor due to the extra computational cost involved in running these simulations, the statistics compare well to those generated by the smaller systems. Angular and kinetic energy distributions are very similar, as are the distributions of atoms sputtered per ion. However the calculated sputtering yields differed by roughly 6-12 %. Distributions of transition barriers were also similar. In the case of the smaller systems the topography we observe the formation of a few large features that saturate the surface, for example a large hillock and deep crater. In the larger surface simulations more features are able to form. We need to model bigger systems over longer times to really understand facet development on high index crystal surfaces.
Chapter 7

Conclusions and Future Work

Throughout this thesis the development of surface topographies under different bombardment conditions has been investigated.

To begin with high energy, swift heavy ion impacts were simulated on a simple MgO system and a specific HfO$_2$ - MgO system, in an attempt to understand experimental results. Initial single atom and cluster impacts on the interface produced interesting results, highlighting the radiation tolerance of the interface. In the case of cluster impacts across the MgO free surface we observed vibrations in the MgO layer but not the HfO$_2$ layer, due to the large difference in mass between Hf and Mg. Two separate models were presented for swift heavy ion bombardment: a MD thermal spike model and a charge stripping model. Both models were shown to produce surface features similar to those observed experimentally (hillocks) and also showed the formation of subsurface ion tracks around the trajectory of the particle. Following the ion impact we saw a high speed wave of kinetic energy spreading through the systems in all cases and a core melted region forms around the ion path. High cooling rates were observed in this region, leading to the formation of an amorphous track region. It was shown that, over the range of models and parameters that were chosen and the different system sizes, the hillock height increases linearly with the stopping force of the ion, as does the sputtering yield. Interestingly, in all simulations involving a HfO$_2$ free surface
we observed the formation of a network structure on the surface. This reconstruction forms as a result of our technique for creating a free surface. It is unclear if this is an artefact of the potential or a real result.

In the second results chapter a model was developed for simulating bullet impacts on SiC (as used in armour plating). The model produced features in line with those seen experimentally. For example we observed material in the zone around the bullet flowing out of the lattice or onto the surface. Impacts on both the 4H and 6H polytypes were considered. When comparing the two polytypes we saw less defects form in the 4H system than in the 6H system, for identical bombardment conditions. This suggests the 4H system could be more resistant to bullet impacts. However we also observed the propagation of dislocations in the 4H system, a feature that did not occur in any 6H systems. Very little sputtering was observed during the 4H simulation or the lower speed 6H simulation. Some large clusters were ejected during the smaller bullet impact on 6H system. However, increasing the size of the bullet (and the system) lead to a large increase of sputtering, with many large, fast moving and high temperature clusters forming in this case. In each case a cap is seen to form over the entry point of the bullet in the material. These features are similar to the hillocks that form over ion tracks in the much higher energy particle bombardments studied in the previous chapter. As in the previous chapter we also observe a wave of kinetic energy from the point of impact of the bullet on the material. The speed of this wave was similar in all simulations.

The final two results chapters both modelled the erosion of an Au substrate subjected to multiple low energy particle bombardments, using different methodologies. The first of these chapters implemented a traditional MD based approach to modelling successive impacts. 5 keV Au impacts were considered on Au systems at normal incidence and an angle of incidence of 60°. The surface orientation in this chapter was \{3\,1\,1\,0\}, similar to the \{3\,1\,1\,1\} orientation that has been shown to produce interesting features experimentally. Using the traditional model many of these features were reproduced, including etch pits with faceted edges and
hillocks on the surface. However our calculated sputtering yields were higher than those obtained experimentally, even when using a larger system, which suggests that either the systems were too small or the methodology not adequate. We also observed a build up of defects throughout the simulations. This was due to the really high dose rate that the MD methodology gives: a new impact was occurring every 20 ps. This does not allow diffusion events to occur between impacts, since they happen over much longer time scales.

In order to overcome these weaknesses in the traditional MD methodology chapter, a new hybrid technique was presented in the final results chapter. This technique still used MD for the ballistic phase but then used on-the-fly kinetic Monte Carlo to model diffusion between bombardments, over much longer time scales. Simulation times were of the order of seconds. Normal incidence impacts across both \{3 11 0\} and \{0 1 0\} orientated surfaces were considered, at a lower energy of 500 eV. Calculated sputtering yields were in line with those found experimentally. In all cases we observed the same erosion process. Under bombardment a rough topography forms which eventually stabilises. We see oscillations in the surface roughness as the surface heals between impact events, by way of surface diffusion. The same thing occurs below the surface. We observe the formation of subsurface interstitial loops. Smaller loops, up to 5 atoms in size, can diffuse through the lattice, whereas larger loops remain immobile until they are annihilated by subsequent bombardments. The cycle of formation and annihilation of these subsurface defects continues throughout the simulations. We do not observe a build up of subsurface defects, as seen in the previous chapter. In this chapter Ar as well as Au bombardment was considered. In the case of Ar bombardment we observed a much higher number of low energy transition barriers for diffusion between impacts. This was a result of subsurface implanted Ar atoms diffusing through the system and considerably slowed the time advancement of the simulation. These implanted Ar atoms would remain in the system until they became exposed as the surface erodes, or they diffuse to the surface and out of the system. We observed small clusters of up to three Ar atoms forming in voids in the lattice (a result of the particle bombardment). At higher temperatures
it may be possible for larger bubbles to form.

7.1 Future work

The original aim of modelling the formation of “surface spires” in the HfO$_2$ - MgO interface (see Figure 3.1) was not achieved. This could be due to a number of factors, one of which is the difference in length scales. The structures in the experimental work were of the order of microns in size and it is possible they do not scale to systems of the size we were able to model. However our models did produce features seen experimentally and it is likely that further work on larger systems and different model parameters could lead to an explanation for the experimental findings: the simulations on the largest system produced results closer to those seen experimentally, with crater formation but no raised central regions. Also it would be useful to do some work on better understanding the half life parameter in the charge stripping model. A variable charge potential would also enable more accurate modelling of the free surface.

With respect to the bullet impact simulations it would be worthwhile to investigate a wider range of parameters, such as larger bullets and varying the speeds. As computers become more powerful it becomes easier to model larger systems, which is of key importance to this investigation.

In order to fully understand the formation of features, such as faceted etch pits and pyramids, on metal surfaces bombarded by low energy ions, larger systems need to be considered. It was also be interesting to model oblique incidence angle bombardment using this model.

To speed up calculations in the MD code it would be useful to incorporate CUDA programming into the current Fortran code. This could lead to a large speed up in expensive areas such as the neighbour list calculation. The on-the-fly kinetic Monte Carlo code would also benefit from being rewritten in a more modular format, which would make it easier to expand the code and also to optimise it.
References


