Modelling Growth of Rutile TiO₂

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Modelling Growth of Rutile TiO$_2$

Louis J. Vernon

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Doctor of Philosophy of Loughborough University

April 30, 2010
Abstract

TiO$_2$ is a well investigated material due to its vast array of applications, from the most common white food colouring, to usage as an optical coating due to its high refractive index. When deposited as a thin film for use in solar control coatings using a magnetron sputtering device, TiO$_2$ is found to form in rutile, anatase and amorphous phases, with the rutile (1 1 0) and anatase (1 0 0) crystal surfaces occurring most frequently. While the influence of deposition rate, substrate bias voltage, oxygen partial pressure and temperature have all been investigated experimentally, there are fewer simulated results. This seems to be primarily due to the lack of a suitable empirical potential through which dynamics can be accurately modelled. In this research project, the short-comings of the leading fixed and variable charge TiO$_2$ potentials were revealed through comparison of binding energies and transition barriers for simple ad-clusters and interstitials to DFT. This led to the development of an improved variable charge potential, particularly when modelling the rutile (1 1 0) surface.

It has been experimentally demonstrated that rutile growth results in a reduced surface due to the formation of large numbers of Ti interstitials and this was also suggested due to low Ti interstitial formation barriers found using DFT and the variable charge empirical potentials. The high interstitial formation probability was confirmed when performing large numbers of Ti$_x$O$_y$ depositions at typical industrial energies. Correlations between impact site and numbers of interstitials and vacancies formed were found along with insight into typical penetration depths and common defect structures.

Multilayer growth was successfully modelled using classical MD by accelerating the deposition rate. The large numbers of formed interstitials coupled with a high escape barrier resulted in defective growth and so it was necessary to increase the substrate temperature such that atoms were mobile on the computational time-scale. Multilayer growth was investigated as a function of deposition energy, cluster composition and stoichiometry on the rutile (1 1 0), anatase (1 0 0) and amorphous surfaces. The optimum conditions for forming defect free rutile were found along with more limited insight into the ideal growth conditions when depositing on anatase and amorphous substrates. Finally a long time-scale dynamics technique, the ‘on-fly-kinetic Monte Carlo’ method, was developed, and using an efficient bespoke transition search algorithm, rutile TiO$_2$ growth was successfully modelled at 350 K, with some caveats to avoid becoming entrenched in low activation diffusion processes. The final conclusion being that low energy depositions of large clusters with an oxygen excess would produce optimum film growth.
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Chapter 1

Introduction

The field of material science was founded on a bedrock of experimental study. As technology has progressed our understanding of the microscopic properties that govern the holistic nature of materials has vastly improved through the use of modern techniques such as diffraction [69], which allows insight into the crystallography of a material, and spectroscopy [61] which allows accurate molecular and composition analysis. While technology has improved to the point that it is possible to resolve individual atoms on the surface of a material using a scanning tunnelling microscope [11] there are often situations where such experimental analysis is inconvenient. The cost of the equipment and the materials being investigated can be prohibitively high and sometimes it is impossible to perform a thorough experimental analysis of behaviour due to the hazardous nature of the materials of interest. Often it is impossible to experimentally observe dynamics without influencing the processes of interest. For example, when investigating thin-film growth it is difficult to determine the surface composition without effecting the incident plasma. It has also traditionally been difficult to experimentally capture processes that occur on extremely short time-scales. Recent applications of lasers capable of attosecond pulses could make extremely brief processes theoretically observable, however, it is still difficult to capture them [54].

Throughout our history mathematical models have been derived to describe physical processes. Through witnessing a small subset of experimental behaviour it is possible to formulate a mathematical expression which attempts to satisfy all the experimentally obtained information while allowing extrapolation of the model to predict behaviour outside of the investigated domain. Traditionally mathematical models involve a reduction of a complex system; models that govern the bulk modulus,
elastic constants or temperature governed behaviour are usually functions of a few variables that can be calculated in a straightforward fashion. In practice these properties are a function of the interaction of millions of atoms and until recently modelling these interactions to ascertain macroscopic behaviour has been beyond the scope of material science researchers.

With the advent of the computer age it has become feasible for the first time to reduce the scale of the mathematical model such that modelling can occur at a fundamental level, whilst still obtaining information regarding the holistic behaviour. Computers are the perfect tool for rapidly performing the millions of calculations required to simulate the interactions between atoms to provide bulk behaviour. However, despite Moore’s law and the progressive increase in computer power, the number of calculations that can be performed are still limited such that it is necessary to optimise the model to best suit the problem of interest. An example of model optimisation is multiscale modelling which is schematically demonstrated in Figure 1.1.

Figure 1.1: The type of modelling that is performed is usually determined by the time and length scale of interest. Adapted from from [70].

Some of the most accurate and versatile methods are ‘ab initio’ [43] techniques which require no assumptions regarding interatomic interactions as they calculate the interactions from first principles quantum mechanics. Of the ‘ab initio’ methods, density functional theory (DFT) [51] is particularly
1.1. Research Goals

It is the thin film deposition of TiO$_2$ that motivates this project, particularly when deposited using a magnetron sputtering device. There have been a number of investigations into the composition of TiO$_2$ as a function of sputtering parameters, which have generally concentrated on the composition of the atmosphere through which the depositing particles pass, and the frequency of the pulsed magnetron. It has, however, been difficult to gain a direct insight into the actual mechanics behind popular due to its relatively rapid performance and good accuracy. Unfortunately due to the computational overhead DFT can only be used to model 100’s of atoms or fewer and molecular dynamics simulations that evolve the system in the time domain are very brief compared to other modelling techniques. While DFT is not suitable for the molecular dynamics modelling required within this research project, it has been used to provide a benchmark when parameterising the empirical potentials.

Following on from ‘ab initio’ methods there are 2 empirical based classes of techniques which cover a broad range in both the time and length domain. Empirical potentials differ from the ‘ab initio’ approach in that information regarding minimum energy structural configurations is generally used to parameterise the model. Within the first performance group of empirical potentials there are methods that involve complex many-body components or long range pair-wise interactions, such as when performing electrostatic force calculations. The potentials employed in this research project fall into the first empirical category. As empirical potentials are simplified such that the interaction is merely a function of short-range pair-wise atomic separation, it becomes possible to expand to greater times and system sizes.

Once we approach the $10^{-7}$ m length and $10^{-6}$ s time-scale it is necessary to move towards methods such as finite element techniques [76], that no longer model individual atoms. These models can be excellent for investigating effects such as strain, shear, pressure and delamination, however, are not pertinent to this research project.

A superset of all methods is long time-scale dynamics which allows the previously defined techniques to be accelerated through approximations in the probabilistic dynamics. Some long time-scale techniques were employed in this research project and are described in greater detail in Chapter 5.

1.1 Research Goals
the growth process. It has been experimentally determined that large numbers of Ti interstitials are formed during growth and that the exposure of defective surfaces to an oxygen excess results in surface oxidisation and the formation of stoichiometric, crystalline layers, however, the actual mechanisms that drive this reconstruction are not well understood.

It is the goal of this research project to acquire a direct understanding of the growth mechanisms that result in crystalline TiO$_2$ such that the optimum parameters for growth can be understood. The parameters which will be simulated are the substrate temperature, the cluster deposition energy, which is an analogue of the bias voltage, and the cluster size and stoichiometry, which is related to the oxygen partial pressure and magnetron frequency.

There are two forms of widely used TiO$_2$ potentials; fixed charge and variable charge. Fixed charge potentials have been around for longer, offer far superior computational performance and have been shown to provide excellent values for many bulk attributes of TiO$_2$. Variable charge potentials have a significant computational overhead but offer improved accuracy when dealing with interfaces and surfaces along with non-stoichiometric structures. In the ‘Barriers and Binding Sites’ chapter the performance of one of the commonly used fixed charge potentials, the Matsui and Akaogi implementation [63], is compared to one of the most recent variable charge potentials, the Hallil et al. [41] SMB-QEq. A large number of surface binding sites for Ti, TiO, O, O$_2$ and TiO$_2$ clusters along with interstitial sites are investigated, with the results compared to equivalent simulations using DFT. Transitions between configurations are found using a combination of human intuition, to determine the end state, and transition finding algorithms including the Dimer method [46] and an efficient home grown technique - the relaxation and translation method (RAT) where the end state is not predefined. Transition barriers are calculated using the nudged elastic band method (NEB) [42] and compared to DFT results, which reveals the importance of the O$_2$ bond, something that neither of the empirical potentials reproduce. A modified variable charge (MQEq) potential is developed to reproduce the O$_2$ bond along with improvements to cluster binding energy through reparameterisation of the oxygen hardness, and is found to provide the most accurate behaviour of all 3 empirical potentials when compared to DFT results and therefore forms the basis of further investigations in the later chapters.

The ‘Single Molecule Deposition’ chapter moves the simulations into territory where DFT simulation is very difficult, modelling molecular dynamics. In order to understand the most commonly formed defects as a function of impinging cluster type and deposition energy, 20,000 depositions
are performed on the rutile (110) surface. The depositions are performed on a symmetrically irre-
ducible area and the results are broken down into various statistical attributes including: numbers
of interstitials, vacancies, reflected and sputtered atoms along with the relative composition of Ti
and oxygen where appropriate. The peak penetration depth of interstitials is recorded, along with
histogramic data regarding the numbers of each defect per deposition. Additionally the damage factor
(number of interstitials plus vacancies) is recorded as a function of incidence and found to have a
correlation for many deposition types. Utilising this data, along with the transition barriers calculated
previously it was possible to make some strong conclusions regarding the likely growth behaviour as a
function of cluster combination and deposition energy. Additionally the representation of defects as
network graphs allows the identification of the most common defect structures, of which the top 10
are analysed.

In the ‘Growth’ chapter the ability of the modified variable charge potential to grow rutile TiO$_2$ is
tested and the simulation succeeds in producing several layers of rutile like growth, albeit with large
numbers of residual interstitials when depositing a stoichiometric mix of clusters. It is hypothesised
that the defective nature of the crystal is likely to be a factor of the high deposition rate relative
to the industrial process. The substrate temperature is increased such that the transition attempt
frequency of a 1 eV barrier is scaled proportionally to the acceleration of the TiO$_2$ flux. Heating the
substrate to 1000 K improves the quality of growth significantly, and the influence of growth as a
function of deposition energy is then reviewed. Results suggest that growth at 40 eV would be highly
defective and this is found to be the case. Using low energy depositions onto a substrate at 1000 K
forms the basis into investigations on the influence of stoichiometry and cluster composition on the
quality of rutile growth with results correlated with the expected behaviour given previous chapters.
Having reviewed growth as a function of various parameters when depositing on a rutile substrate,
growth on an amorphous and anatase substrate is reviewed. Anatase is found to reconstruct at high
temperatures, much like in experimental results [25, 22, 21], and as such the temperature is dropped
to 300 K before sensible behaviour is seen.

Finally growth is modelled using an on-the-fly kinetic Monte Carlo (OTF-KMC) method [48].
While a large number of approximations have to be made in order to boost the computational
efficiency, multi-layer growth is eventually modelled successfully, a triumph of both OTF-KMC as a
long time scale technique and the MQEq as a sensible potential for modelling rutile growth.
This research project is highly successful in its original goals. A good empirical potential is acquired through comparison to DFT results and is successfully applied to modelling growth while achieving an understanding of growth dynamics and the influence of deposition parameters in the process. Finally the potential of the OTF-KMC long time-scale dynamics technique is demonstrated, in providing realistic rutile growth at typical industrial temperatures.

1.2 Program Implementation

Most of the methods mentioned within this thesis were implemented by myself specifically for the research project. These include but are not limited to: The NEB (nudged elastic band), simple string, DHS (Dewar Healy Stewart), ART (activation relaxation technique), dimer and RAT (relaxation and translation) methods, Hessian matrix, eigenvalue and prefactor calculation (using LAPACK), a lattice visualiser and editor, an efficient conjugate gradient minimiser, a cluster deposition injector, LKMC - a comprehensive on-the-fly kinetic Monte Carlo package, a rapid lattice defect detector (using spatial decomposition) and defect cluster analyser using 'nauty' (no automorphisms, yes?). Software I contributed to included the LboMD (Loughborough molecular dynamics) package for which I implemented the Hallil et al. short range interactions, in addition to the potential modifications described within this thesis and the AVA (atomic visualisation and analysis) suite for which the ability to render using POVray and animate using ffmpeg was added. In total over 60,000 lines of Perl, Python and Fortran were written for this project.
Chapter 2

Background

2.1 Titanium Dioxide

Titanium dioxide is a widely used and highly versatile compound, with applications ranging from simple pigmentation for foods to nano-scale optical films. The oxide was originally discovered in 1791 by a clergyman named William Gregor in the rectory of Creed in Cornwall. William Gregor had a strong interest in geology and had stumbled upon a new element which he named ‘manaccanite’. Titanium, in the rutile form, was discovered by Martin Heinrich Klaproth later in 1791, who named it after the Greek Titans, unaware that it had previously been classified. While Gregor retained the credit for the discovery of Titanium, Klaproth’s choice of name stuck.

Widely used as a pigment, TiO$_2$ is referred to as ‘titanium white’ and is the most commonly used white colouring due to a very high refractive index. Titania acts as an excellent UV absorber, forming the primary active ingredient in many suncreams and is also used to protect plastics from UV damage. Used to whiten food, for example in skimmed milk, over 4 million tons of TiO$_2$ are produced purely for pigmentation purposes yearly.

It is not titania’s use as a pigment that motivates this research project. Modern science has allowed us to work with materials at smaller scales than previously imaginable. Materials that were previously well understood at the large scale are found to have new and exciting properties when dealing with them at the nano-scale and titania is one such material. Applied in thin layers of nanometre thickness, TiO$_2$ is transparent while retaining the ability to block UV light, thus making it an excellent candidate for application to glasses for the protection of the wearer’s eyes against
harmful UV radiation from the sun. An additional benefit of TiO$_2$ is the ability to minimise reflection from the surface of glass; it is possible to construct layers of such perfectly controlled thickness that internal reflection produces light half a wavelength out of phase with that incident on the surface, resulting in destructive interference.

Titanium dioxide can be found naturally in 3 polymorphs; rutile and anatase, which have tetragonal structures, and brookite which has an orthorhombic structure. In this research project only the anatase and rutile polymorphs are considered due to the potential formation of both crystal types during thin film deposition. The rutile form of TiO$_2$ occurs more prevalently, particularly at higher temperatures, and often forms with the (1 1 0) preferential surface due to the minimum breakage of ionic bonds. The rutile unit cell is shown in Figure 2.1 with the oxygen atoms highlighted in red, while the Ti atoms are silver. This colour scheme is maintained for the remainder of this thesis.

![Figure 2.1: The TiO$_2$ rutile unit cell, with oxygen atoms shown in red and Ti atoms in silver.](image)

Of more use is the diagram of the rutile lattice (1 1 0) surface shown in Figure 2.2. There are several important features that will be referred to throughout this thesis that the reader needs to become familiar with. The most obvious feature of the (1 1 0) surface is the oxygen ad-row which runs in the [1 1 0] direction. The region between the oxygen ad-rows is known as the trench which runs parallel to the oxygen ad-row. The Ti atom that sits in the centre of the trench is known as the 5-fold co-ordinated Ti, as it is bonded to 4 neighbouring oxygen atoms within the trench, referred to as surface oxygen atoms, and a single oxygen atom directly beneath it. A second unique Ti site is
directly between successive ad-row oxygen atoms and is called the 6-fold co-ordinated Ti atom due to 6 neighbouring oxygen atoms, consisting of 2 ad-row oxygen atoms, 2 surface oxygen atoms and 2 sub-surface oxygen atoms. With knowledge of these reference points it is possible to comprehend the description of all defects and binding sites later in the thesis.

![Figure 2.2: The rutile (1 1 0) surface in schematic profile (referenced from [24]) and rendered perspective form.](image)

A major concern with thin films applied to glass is durability. When applied to window glass, before transportation to remote sites for installation in buildings, the current technique is to spray glass sheets with microscopic polymer beads which act to minimise damage that glass sheets experience during the shipping process. Unfortunately the beads occasionally scratch the coating and therefore ruin the glass, requiring replacement which is an expensive process. When TiO$_2$ is typically deposited it forms an amorphous structure with little crystallinity and a hardness of 5-6 GPa [92], softer than the glass substrate. If it was possible to control the deposition process such that rutile TiO$_2$ was formed this would increase the hardness of the coating to 8 GPa or greater, improving the durability and longevity of the coating with little detriment to the optical properties.

A perspective view of the anatase (1 0 0) surface is shown in Figure 2.3. It is not necessary to define the individual atomic sites within the anatase structure as they will not be closely investigated,
however, the substrate will form the basis for some growth modelling later in the project.

![Figure 2.3: The anatase (1 0 0) surface in schematic profile and rendered perspective form.](image)

The anatase polymorph of TiO$_2$ has properties that allow it to be used as the primary agent of self-cleaning glass. UV light incident on the TiO$_2$ anatase structure produces free radicals that are able to break down organic compounds on the surface of the glass. Additionally anatase is hydrophilic attracting water to the surface such that it slides down the surface of the glass in sheets rather than beads providing optimum cleaning.

TiO$_2$ often forms part of a multilayer stack containing different materials which all serve a purpose. A typical stack might also contain a thin silver layer with a thickness of about 8-10 nm sandwiched between two ZnO layers, due to silver’s ability to reflect infra-red light allowing buildings to remain cool during the summer and keep heat in during the winter.

![Figure 2.4: An example commercial solar control coating [16]. Here the TiO$_2$ serves in a bonding and anti-reflective capacity.](image)
2.2 Magnetron Sputtering

The primary means of forming nanoscale multilayers on glass is magnetron sputtering, which is simulated within this research project. The magnetron sputtering device uses ions to sputter atoms from our ‘target’, the material, which we intend to deposit, onto the ‘substrate’, glass covered in a number of previously deposited coatings. The deposition chamber contains a low pressure mix of oxygen and argon, an example ratio would be 1:9, with the oxygen atoms allowing Ti to oxidise on the way to the substrate. Strong magnets create a magnetic field around the target and when a high voltage is applied the argon gas becomes ionised thus forming a plasma along the electric field. Inside the plasma the argon atoms become positively charged creating secondary free electrons. The ions continually bombard the target, sputtering atoms which are accelerated towards the substrate due to a bias voltage. Typical kinetic energies seen during the industrial layer growth process correspond to the region of 10-40 eV [89] and as such those energies provide the basis for depositions within this research project.

![Figure 2.5: Schematic of a magnetron sputtering device with an argon plasma bombarding the target to sputter atoms onto the substrate. Referenced from [66].](image)

A common issue with magnetrons is the build up of charge in local insulating regions which results in the formation of a molten target region with the production of large particles, influencing film growth roughness and crystallinity. A simple means of dealing with this issue is to detect the
formation of arcs and to reduce the power available such that the arc does to cause damage, however, this effects the growth rate. An advancement in magnetron sputtering has led to the creation of pulsed magnetrons; these prevent the formation of localised charge through brief negative pulses. It is through the use of pulsed magnetron sputtering devices that it is possible to form crystalline TiO$_2$ thin films.

2.3 Previous Work

2.3.1 Experimental

While it is difficult to gain an insight into the precise growth dynamics due to scale, there have been many studies which provide information regarding the macroscopic growth of titania and are relevant to this research project.

Early investigations into the composition of TiO$_2$ films grown using sputtering found that the surfaces were non-stoichiometric, demonstrating a progressive reduction of oxygen during the growth process [55]. It was originally and mistakenly assumed that the oxygen deficiency was due to large numbers of oxygen vacancies and it was not until 1999 that Henderson demonstrated that the imbalance was due to a prevalence of Ti interstitial atoms [44].

Several groups investigated the influence of increasing temperature on surface composition using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) and it was recognised early on that the stoichiometry and structure of deposited films were restored as the temperature was increased. Tait and Kasowski demonstrated that between 473 and 873 K complete restoration of the TiO$_2$ rutile stoichiometry could be achieved [97, 18], however due to misinterpretation of the source of the stoichiometry imbalance it was assumed that the defects were annealed through diffusion of oxygen vacancies. Chung et al. [18] found that the TiO$_2$ surface could be annealed even without the presence of an oxygen gas at the cost of amorphising the bulk although once again incorrectly assumed that this was due to the diffusion of oxygen vacancies into the bulk rather than Ti interstitial atoms. Despite early conclusions that oxygen vacancies were the primary defect, the interstitial relaxation site and corresponding diffusion mechanisms had been described early on by Huntington and Sullivan in 1965 [52] who correctly identified the exchange based diffusion process, however the energy barriers associated with the diffusion mechanisms were assumed to be greater than those for
the oxygen vacancy.

Onishi and Iwasawa performed the first atomic scale visualisations of the TiO$_2$ recovery process [73]. Having prepared a TiO$_2$ (1 1 0) surface through argon sputtering they used a scanning tunnelling microscope (STM) to observe the influence of an oxygen atmosphere on the reduced surface at an elevated temperature of 800 K. They observed that the introduction of an oxygen atmosphere allowed for the complete reoxidisation of the surface through annealing Ti interstitials until the supply of interstitial ions was exhausted. This was achieved by oxygen ad-atoms which appeared to bind in the [1 0 0] trenches, drawing the interstitial atoms onto the surface, as shown in Figure 2.6.

![Figure 2.6: The rutile (1 1 0) surface imaged using STM. The presence of oxygen causes the surface to anneal with oxygen ad-atoms binding above 5-fold coordinated Ti atoms, pulling Ti interstitials from the bulk. Referenced from [73].](image)

Also using an STM, Min Li et al. steadily increased the temperature from 370-830 K to ascertain the rate at which the oxidisation of the Ti interstitials occured [60]. By then examining the temperatures at which Arrhenius behaviour was observed (<530K) it was possible to deduce an interstitial escape barrier of 0.82 eV. Despite the current conclusion that TiO$_2$ reduction is dominated by Ti interstitials,
oxygen vacancies have been observed using STM, however they are located on the ad-rows within the rutile (1 1 0) surface and have been found to play no significant role in the growth behaviour as they are quickly saturated [12].

2.3.2 Simulation

Before any form of sensible simulation can be performed it is necessary to derive a potential that produces sensible behaviour. There have been a large number of potentials which sought to provide realistic behaviour when modelling TiO$_2$, particularly in the rutile phase, almost all of which aim to model the stoichiometric structure. The physical properties of TiO$_2$ were well established early on due to the ease with which rutile crystal could be grown experimentally. These attributes would normally assist with the construction of potentials to model the rutile phase, however it was not until 1982 that Sawatari and Iguchi investigated the formation energies of point defects in rutile [88] using the shell model. The authors surmised that the lack of prior simulated calculations was due to confusion regarding the composition and nature of defects in reduced rutile. It is interesting to note that using their model Sawatari and Iguchi found that the formation energy of an oxygen vacancy at 10.1 eV was far higher than experimentally predicted values which ranged from 3.9-5.6 eV. They go on to question the reliability of experimental data and correctly suggest that any oxygen vacancies that form would be unstable.

In 1996 Collins and Smith investigated nine Ti-O potentials, modelling 3 different TiO$_2$ polymorphs and found that most provided poor overall agreement with experimental results when calculating lattice energy and lattice and elastic constants [19]. Of the 9 potentials they recommended only the Matsui and Akaogi potential along with one they had developed. The Matsui and Akaogi [63] implementation has been repeatedly shown to provide excellent performance [99, 94, 29] in terms of bulk properties, despite the implementation of many other empirical potentials since its inception. While this fixed, partial charge potential has been shown to be particularly good at reproducing the correct lattice parameters and bulk moduli of the three common polymorphs of titania, it deals poorly with non-stoichiometric configurations. In addition to struggling with stoichiometry issues, it is clear that fixed-charge potentials will have problems when dealing with interfaces and surfaces, due to the full bulk charge resident on the surface atoms. As such a means for intelligently varying the charges is desirable.
In 1991 Rappé and Goddard [81] proposed a means for allowing the charge distribution to vary within a lattice as a function of atomic environment, which allowed the production of various charge equilibrating (QEq) potentials, including those for TiO$_2$. In 2006 Hallil et al., identified issues with proceeding TiO$_2$ variable charge potentials utilising the QEq scheme, finding that the previously suggested short-range oxygen-oxygen and titanium-oxygen interactions were unsuitable due to unphysical long-range forces and an inability to reproduce the correct defect energies. The modification of the oxygen-oxygen short-range potential along with the introduction of an N-body titanium-oxygen interaction resolved the majority of issues providing improved relaxation configurations, however, it was recognised that there were issues with the degree of charge transfer in the neighbourhood of defects. Thomas and Marks [98] specifically questioned the Hallil et al. modifications to the previous QEq implementations, stating that the forces were dominated by the short-range interactions, with the electrostatic component playing a relatively insignificant part. Comparing 5 current QEq based TiO$_2$ potentials and a modified Matsui and Akaogi potential, Thomas and Marks found that when relaxing a Ti$_3$O$_5$ lattice the Matsui potential provided the optimum behaviour while the Hallil et al. potential performed the worst. As this research project deals with configurations that are close to the standard TiO$_2$ stoichiometry the Matsui and Akaogi potential will provide the basis for investigations into behaviour using a fixed charge potential, while the Hallil et al. SMB-QEq (second-moment Morse Buckingham) potential will provide the basis for investigation into behaviour of particle bombardment where variable charge is important.

In addition to the early work by Sawatari and Iguchi there have been a number of more recent studies that investigate the binding energies and barriers associated with point defects in the rutile structure. Cho et al. investigated the formation energy for both the Ti interstitial and oxygen vacancy using DFT, finding formation energies of 7.09 and 4.44 eV respectively, although they acknowledge the oxygen binding energy is subject to size effects [17]. More recently Mulheran et al. also used the Hallil et al. variable charge potential as the foundation for their investigation into binding energies and transition barriers on the rutile (1 1 0) surface [68]. Comparing results to DFT+U they found that the binding energy for the Ti interstitial was overestimated by 1.88 eV thus rendering potential growth dynamics highly unrealistic. Using Bader analysis [86] to investigate the degree of charge transfer witnessed when using the DFT+U model, Mulheran et al. identified excessive charge transfer on the oxygen atoms as the primary cause of the overestimation in binding energy and acted to
resolve the issue through fixing the charges on the oxygen atoms. Through fixing the oxygen charge they were able to reduce their predicted Ti interstitial escape barrier from 3.31 to 1.41 eV almost perfectly correlating with the DFT+U predicted barrier. Unfortunately fixing the oxygen charge introduces new issues to potential dynamics; the Ti surface diffusion barriers drop significantly and any sputtered or reflected oxygen atoms will not have their charges diminished as they leave the lattice. It is also not entirely clear that DFT+U is the best ‘ab initio’ model for simulated surface dynamics and the optimised Ti interstitial barrier could potentially be incorrect. However, it seems that prior to this research project Mulheran’s implementation is the most promising for modelling growth dynamics on rutile (110).
Chapter 3

Simulation Methods

This chapter introduces molecular dynamics (MD) and explains how a computer can be used to simulate a number of atoms using Newton’s 2nd law of motion. After an introduction to simulation methods and an explanation of the mechanism with which one is able to evolve the set of atoms in the time domain, the specifics of the potential functions describing the atomic behaviour relevant to this particular research project are given. Constraints of the simulation are also discussed along with some performance optimisation methods which are vital for achieving useful simulation time-scales.

3.1 Introduction

Science depends on finding order in the chaos, the ability to find patterns of behaviour in results that allow us to ascertain some predictability in the behaviour from which we can derive models to extrapolate the behaviour. Traditionally these functional models are limited to making singular static extrapolated predictions, however with the advent of powerful computers it becomes possible to let the functional models drive the research. Rather than making the predictive behaviour a passive component we can use simulation to find results which can then be checked by experiment. Even more exciting, we can perform simulations that allow us to investigate behaviour that is beyond our capability to reproduce experimentally.

The first simplistic molecular dynamics simulations were performed in the 1950s, treating atomic collisions as hard spheres [4], however the first simulation that bears a realistic resemblance to modern day molecular dynamics was the modelling of liquid argon using a Lennard-Jones potential [53] by
Rahman [79] in 1964. Since then, correlating with Moore’s law, the rapid explosion in computer power has allowed us to expand from modelling 100s of atoms to millions of atoms when using simple pair potentials. However, there are still limitations to what we are able to simulate. Whilst millions of atoms can be modelled, the time-scale must remain relatively small due to computational constraints with simulations typically in the pico to nanosecond time range. Further, while performance optimisation methods allow the number of atoms, \( n \), to be increased without incurring an \( n^2 \) order computational cost, this is dependent on the termination distance, \( r \), of interaction between atoms. As such ionic systems with an interaction energy that decays as \( \frac{1}{r} \) scale significantly worse and are limited to small systems or short simulation time-scales, unless special methods are used.

In order to perform a molecular dynamics simulation the underlying software must provide two distinct functions. A means with which to evolve the system in the time domain is required, given position and force information for each atom, along with a potential function which determines the interaction force. Whilst the potential function is dependant on the particular system we are modelling, the time integrator remains common to all molecular dynamics simulations.

### 3.2 Time Integration

A variety of time integrators are available to molecular dynamics developers. A straightforward candidate might be the Euler method [59] which is computationally lightweight however too inaccurate for the purposes of molecular dynamics where conservation of energy is vital. The LBOMD (Loughborough molecular dynamics) package used to perform the simulations described in this thesis uses the velocity Verlet [96] algorithm which provides a good compromise between accuracy and computational performance. The velocity Verlet algorithm is a second order method that evolves the simulation at each step by numerically integrating Newton’s equations of motion and is given by:

\[
\mathbf{r}_i^{\Delta t[k+1]} = \mathbf{r}_i^{\Delta t[k]} + \mathbf{v}_i^{\Delta t[k]} \Delta t + \frac{\mathbf{F}_i^{\Delta t[k]} (\Delta t)^2}{2m_i} \\
\mathbf{v}_i^{\Delta t[k+1]} = \mathbf{v}_i^{\Delta t[k]} + \left( \frac{\mathbf{F}_i^{\Delta t[k]} + \mathbf{F}_i^{\Delta t[k+1]}}{2m_i} \right) \Delta t
\]

where \( \mathbf{F}_i^{\Delta t[k]} \) is the force vector acting upon the atom \( i \), \( m_i \) is the mass of \( i \), \( \Delta t \) is the time-step and \( \Delta t[k] \) is the current time. The global error in the position and velocity are \( O(\Delta t^2) \) when using the
velocity Verlet algorithm and as such the accuracy of the simulation is determined by the size of $\Delta t$. A small time-step, for example $10^{-16}$ s, ensures excellent conservation of energy with poor simulation performance while a larger time-step, such as $10^{-14}$ s, provides rapid simulation times with poor energy conservation. It is clear that energy conservation is dependent on the magnitude of movement of the atoms between force evaluations. Thus for a specific level of accuracy the time-step needs to vary as a function of the maximum velocity. The scheme LBOMD uses makes the time-step dependent on the maximum KE within the system and the distance of closest approach, with a typical time-step of $10^{-15}$ s. The Beeman [9] method is another commonly used MD time integrator which provides $O(\Delta t^3)$ accuracy per step at the cost of an additional computational step and greater memory usage.

### 3.3 Interatomic Potentials

The velocity Verlet algorithm provides a means with which to evolve the system in the time domain, once the dependence on the force vector acting on every atom is known. Ideally ‘ab initio’ [43] force calculations would be performed, solving the Schrödinger equation for the current simulated atomic structure on the fly. ‘Ab initio’ simulations provide a high level of accuracy and can deal with complex atomic interactions that classical potentials can sometimes struggle to approximate. Unfortunately this sort of modelling is very computationally expensive and therefore largely impractical for molecular dynamics of the scope covered in this thesis.

As computers have become more powerful and ‘ab initio’ modelling becomes more accessible it is often useful to use ‘ab initio’ modelling to parameterise the empirical potential function in order to provide more accurate results. Another approach could be to avoid predefining an analytical form altogether by using some rudimentary AI technique, such as neural networks or genetic programming, to derive the best function to match a specified experimental or ‘ab initio’ derived dataset [85]. However, traditionally the derivation of a function to describe the interatomic behaviour is based on deciding a fixed analytical functional form and using experimental data to parameterise the function. The simplest form of traditional potential is a pairwise function $V(r_{ij})$ which for a given pair of atoms $i$ and $j$ is dependent on the separation $r_{ij}$. The energy $E_i$ of atom $i$ being given by the sum over all pairs of $ij$:

$$E_i = \frac{1}{2} \sum_{i \neq j} V(r_{ij})$$
3.3. INTERATOMIC POTENTIALS

Pair potentials are very popular due to their simple nature, being easy to implement and quick to parameterise. However for many materials a pair potential is not satisfactory to provide the full range of interactions. For close particle separation, screened Coulomb pair potentials have been shown to be very useful; there is one potential, the Ziegler-Biersack-Littmark (ZBL) [103] potential which has become a sort of ‘industry standard’ for all close range interactions between atoms.

3.3.1 ZBL

As two atoms approach each other their respective electron clouds cease to screen the positively charged nuclei from one another resulting in an increasing Coulombic repulsive potential $V_{r_{ij}}^{q}$ shown in Equation 3.3 where $Z_i$ and $Z_j$ are the atomic numbers of atoms $i$ and $j$ respectively, $q$ is the elementary unit of charge and $\phi(x)$ represents the screening of the electron cloud and ranges from 0 to 1.

$$V_{r_{ij}}^{q} = \frac{q}{4\pi\epsilon_0} \frac{Z_iZ_j}{r_{ij}} \phi(x)$$

Equation 3.3

Ziegler, Biersack and Littmark were able to deduce the repulsive potential for 522 pairs of atoms from their scattering angle and used the data to derive the universal screening potential in Equation 3.4 which is accurate to approximately 18% for energies over 2eV. $x$ is a dimensionless scaled radius given in Equation 3.5.

$$\phi(x) = 0.1818 \cdot e^{-3.2x} + 0.5099 \cdot e^{-0.9432x} + 0.2802 \cdot e^{-0.4028x} + 0.02817 \cdot e^{-0.2016x}$$

Equation 3.4

$$x = \frac{r_{ij}}{0.8854} \cdot \frac{Z_i^{0.23} + Z_j^{0.23}}{0.529}$$

Equation 3.5

In this formula, the separation $r_{ij}$ has units of Ångströms. The ZBL pair potential is implemented for all atomic interactions where $r_{ij}$ is typically less than 1.5 Å. In order to conserve energy the introduction of the ZBL function to the atomic interaction needs to be smooth and so a screening function is used to progressively switch on the ZBL as a function of the interatomic separation. A typical cosine screening function is shown in Equation 3.6, which has zero 1st derivatives at the points.
\(x_1 \) and \(x_2\), required for conservation of energy.

\[
S(r_{ij}) = 1 + \cos\left(\frac{\pi}{2} \frac{x_1 - x_2}{r_{ij} - x_1}\right)
\]  

(3.6)

Using a screening range of 1 to 1.5 Å, Figure 3.1 demonstrates the effect of the screening function applied to the ZBL potential for 2 Ti atoms. The cosine screening function has been scaled by 140 to allow it to be plotted on the same scale.

Figure 3.1: The potential energy for the ZBL potential due to two Ti atoms and the screened ZBL with a scaled cosine screening function.

In addition to smoothing the ZBL to zero at a finite distance, a similar cosine splining function is used to switch between potential functions as we move from nuclei driven repulsive Coulombic to a more typical chemical potential.

### 3.3.2 Lennard-Jones Potential

Another commonly used pair potential is the Lennard-Jones interaction [53]. Despite being one of the earliest atomic interactions proposed, the LJ potential has been successfully applied to model the motion of atoms in Argon and other gasses [79]. The form of the LJ potential is given below:

\[
V_{r_{ij}} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]
\]

(3.7)

where the 12th power term constitutes a short range Pauli repulsion interaction and the 6th power
term provides the long range van der Waals attraction. The $\epsilon$ term can be used to tune the binding energy of the particles whilst the $\sigma$ parameter dictates the breadth and location the potential well.

### 3.3.3 TiO$_2$ - M. Matsui, M. Akaogi

Matsui and Akaogi developed the pair potential shown in Equation 3.8. Parameterised to reproduce all 4 polymorphs of TiO$_2$, the potential is widely used [99, 94, 29] and reproduces bulk TiO$_2$ parameters with excellent accuracy.

$$V_{r_{ij}} = \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}} - \frac{C_i C_j}{r_{ij}^6} + f \cdot (B_i + B_j) \cdot e^{\frac{\Delta_i + \Delta_j - r_{ij}}{B_i + B_j}}$$ (3.8)

where $q$ is the effective charge, $A$ the repulsive radius, $B$ the softness parameter and $C$ the Van der Waals coefficient. While $C$ and $q$ were externally derived and remained fixed, $B$ and $A$ were optimised by Matsui and Akaogi to reproduce the optimal lattice parameters. The final form of the potential reproduces the lattice constants to within 2% of the experimental values for all 4 polymorphs whilst having a mean error of only 0.05 Å in the Ti-O separation for rutile.

Unfortunately due to its fixed charge nature the Matsui and Akaogi potential deals poorly with locally non-stoichiometric configurations. Whilst the rutile (1 1 0) terminated surface is stable and relaxes without surface reconstruction, the introduction of a Ti ad-atom leads to considerable surface distortion and/or reconstruction depending on the binding site, rendering the potential inadequate for surface growth.

### 3.3.4 TiO$_2$ - Hallil et al.

The same year that Matsui and Akaogi published their fixed charge potential, Rappé and Goddard published a method for predicting charge variation of atoms within an atomic simulation [81]. This charge equilibrating (QEq) scheme allowed charges to alter dependent on the configuration of the neighbourhood. The charge variation was determined by an energy minimisation procedure. The charge dependent atomic energy or ‘self-energy’ of the ions is given in Equation 3.9.

$$E_i = E_i(0) + \chi_i^0 q_i + \frac{1}{2} J_i^0 q_i^2$$ (3.9)

where $\chi_i^0$ corresponds to the electronegativity, i.e. the desire of the ion to acquire charge, whilst $J_i^0$
3.4 Boundary Conditions

relates to the hardness and acts as a penalty function for acquisition of excess charge. The total energy due to charge including the electrostatic and self-energy terms is minimised at each simulation step using the conjugate gradient method to perform a constrained relaxation such that the sum of the charges is zero.

Hallil et al., formalised the SMB-QEq TiO$_2$ potential using the QEq scheme with hardnesses of 12.162 and 10.572 eV and electronegativities of 7.543 and 0.0 for oxygen and Ti respectively, based on original work by Swamy and Gale [95]. Hallil et al. recognised that the previously proposed Morse repulsive potential was not satisfactory for describing the energy associated with oxygen defects and so introduced an N-body potential [20] that had been previously developed to describe metallic alloys.

The new Ti-O interaction was based on the second moment tight binding approach and attempts to compensate for the covalent energy of the bond.

$$E^i = \sum_j A_{IJ} e^{-P_{IJ}(r_{ij}/r_{ij}^o-1)} - \left( \sum_j \sigma_{IJ}^2 e^{-2q_{IJ}(r_{ij}/r_{ij}^o-1)} \right)^{1/2} \tag{3.10}$$

The first pairwise sum is a Born-Meyer type potential [2] whilst the N-body secondary sum provides the energy contribution from the covalent bond. For the O-O interaction the repulsive component of a Buckingham potential [13] was used.

$$E^{ij} = A_{ij} e^{-\frac{r_{ij}}{\sigma_{ij}}} \tag{3.11}$$

Hallil et al. were interested in molecular statics and so failed to define a Ti-Ti interaction. Whilst this is acceptable for calculating defect binding energies along with lattice attributes, the ability for Ti atoms to pass through each other during molecular dynamics simulations is obviously unphysical and so a repulsive potential was required. The ZBL was used with the cut-off occurring between 1.5 and 2.5Å. By using a short cut-off it was possible to allow dynamical behaviour without effecting the parameterisation of the other interactions derived by Hallil et al..

3.4 Boundary Conditions

While it is currently only possible to simulate of the order of 1000s of atoms using the variable charge model in growth simulations due to computational limitations, it is often desirable to simulate a much
3.4. Fixed Boundary Conditions

The most obvious mechanism to reproduce lattice strain is to fix the atoms on the outside edge of the lattice cell walls. By forcing 2 or 3 layers to remain fixed, an artificial pressure is applied on the internal atoms, simulating the surrounding bulk. Fixed boundary conditions are suitable for modelling single, relatively low energy events near to the centre of the lattice such as collision cascades in a bulk lattice. It is not necessary to fix all lattice edges; by fixing all but one edge it is possible to simulate a surface that behaves as if it is part of a much larger surface upon which low energy depositions can be made along with calculating binding energies, defect formation, etc.

3.4.2 Periodic Boundary Conditions

Fixed boundary conditions are not appropriate for many types of molecular dynamics simulation. Defect diffusion and surface growth are two examples where a moving atom will be inaccurately modelled near the fixed boundary. In these cases it is necessary to use periodic boundary conditions (PBC’s) which allow more flexibility in the simulation. PBC’s work through tessellating the lattice in all periodic directions such that an atom passing through one periodic edge will wrap around and re-enter the lattice from the other side and each atom near an edge will see atoms of the opposing edge as neighbours.

3.4.3 Thermal Boundary Layers

Thermal boundary conditions deal with an additional problem introduced by using a finite-sized lattice. If a real system containing billions of atoms were to be modelled, energy would ultimately be able to dissipate away from the region where energetic processes occur, such as a surface for depositions or the centre of a collision cascade. By using fixed or periodic boundaries the energy is conserved within the small system which will heat rapidly if successive depositions or cascades occur and as such a method is required to remove the energy from the system. The most common technique to achieve this is to attach a thermostat to a layer of atoms such that their motion is
damped or accelerated dependent on whether the temperature of the lattice is above or below the
desired target temperature. The Berendsen thermostat [10], employed in this work, is widely used due
to the rapidity with which it brings a system to the desired target temperature. The degree to which
the Berendsen thermostat scales the velocities of the thermalised atoms is linearly proportional to the
difference between the system temperature and our target temperature. While efficient at quenching
the system to the desired temperature this unfortunately results in a micro-canonical ensemble for
those atoms that are thermalised, as the thermostat suppresses fluctuations in the total kinetic energy.

With simulations performed within a fixed volume, the majority of the simulations in this project
correspond loosely to a micro-canonical ensemble due to the use of the Berendsen thermostat. While
the introduction of additional atoms during the course of various simulations causes discontinuities in
the statistical ensemble, those simulations can be considered to be a series of discrete constant NVE
(fixed number of atoms, volume and energy) ensembles.

3.5 Performance Optimisation

Whilst the previous sections describe the fundamental components required for an MD simulation, in
practice it proves necessary to implement some performance enhancement to enable the simulation
of interesting system sizes. Using even the most simple pairwise potential results in an $O(n^2)$
computational problem unless some optimisation is provided.

Given a pair of atoms $i$ and $j$, for most interatomic potentials there will be a separation $R_{ij}^{max}$ where
the energy due to the $ij$ bond can be considered to be negligible and therefore ignored. Assuming
this, it becomes only necessary to evaluate the potential $V_{ij}$ where $R_{ij} < R_{ij}^{max}$. However unless $R_{ij}^{max}$
is very large the discontinuity in the potential function will lead to a lack of energy conservation.
As such it is necessary to use a cut-off function such as the cosine function demonstrated in Section
3.3.1 to smoothly switch the potential off. Having ascertained a maximum cut-off distance for our
simulation it becomes possible to construct a list of neighbours for each atom such that only the
potential between an atom and the atoms in its neighbour list are evaluated, reducing the problem
to $O(n)$. In practice it is sensible to create a list of all atoms that are closer than $R_{ij}^{max} + \delta$ where
$\delta$ is a skin as shown in Figure 3.2. By including an additional skin of atoms the simulation can
continue running until any atom has moved greater than the skin thickness before re-evaluating all
the neighbour lists.
Figure 3.2: The radius of the dark grey circle demonstrates the maximum interaction distance from the dark atom while the light grey ring demonstrates the skin/buffer that avoids neighbour list reconstruction at every step. Referenced from [93].

While using neighbour lists reduces the problem to $O(n)$ it is impossible to ascertain whether $R_{ij} < R_{ij}^{\text{max}} + \delta$ without evaluating $R_{ij}$ so constructing the neighbour list in the first place is still an $O(n^2)$ operation. However, it is possible to optimise the construction of neighbour lists using spatial decomposition. By decomposing the lattice into cubic cells the dimensions of which are determined by $R_{ij}^{\text{max}}$ as shown in Figure 3.3 it is possible to once again reduce an $O(n^2)$ to an $O(n)$ operation, as for each atom it is only necessary to check the 26 neighbouring cells in addition to its own for neighbours.

Figure 3.3: When an atom has travelled further then the skin thickness a new neighbour list is constructed by evaluating the separation of all atoms in cells neighbouring the dark atom. Referenced from [93].

Thus the problem is reduced to a periodic $O(n)$ spatial decomposition operation followed by an $O(n)$ neighbour list construction problem every time an atom has moved far enough to exit or enter an atoms neighbour list.
3.6 Electrostatic Evaluation

One of the most expensive parts of a molecular dynamics simulation is the evaluation of electrostatic energy and forces. Due to the $\frac{1}{r}$ decay of the electrostatic energy it operates over large distances and cannot be optimised through neighbour lists and spatial decomposition. The SMB-QEq potential is particularly expensive as multiple electrostatic energy evaluations are required during the energy-charge minimisation process at each time-step.

It becomes necessary to evolve a different way to evaluate the electrostatic potential energy and forces on each atom that moves away from the $O(n^2)$ pair evaluation that would traditionally be used. There are two techniques used within this work that do just that; the first is the Distributed Parallel Multipole Tree Algorithm (DPMTA) [80] which applies to non-periodic systems, whilst the second technique, the Ewald method [31], can only be used when using periodic boundary conditions.

3.6.1 Distributed Parallel Multipole Tree Algorithm

DPMTA is a particularly efficient implementation of a class of techniques named ‘fast multipole methods’ [40] that expand on the concept that a cloud of charges will appear as a point charge at a long enough distance. The tree component of the algorithm describes the decomposition of the lattice into cells. Each child atom is assigned to a cell and the global charge and centre of mass is calculated for the parent cell. In the most basic of tree algorithms, for every atom we evaluate the distance a cell is from that atom and if beyond some cut-off distance the cell is treated as a point charge. The use of a point charge is inaccurate unless small cells are used, defeating some of the optimisation of the problem. Warren and Salmon [84] recognised that better accuracy could be achieved by using a multipole expansion at the centre of the cell to describe charge rather than using a single point. Further improvements of the multipole expansion led to the reduction of the $O(n^2)$ to a $O(n)$ problem. DPMTA is a particularly efficient implementation of these methods which has been parallelised to use MPI.

3.6.2 Ewald Method

The Ewald method is used when modelling ionic systems with PBCs. By making assumptions about the periodic nature of the lattice crystal it becomes possible to decompose the electrostatic evaluation into a short range real part along with a long range reciprocal part in Fourier space, providing $O(n^2)$
computational scaling. This limits simulations to 10s of thousands of atoms using a fixed-charge ionic potential and to 100s or 1000s of atoms using a variable-charge potential. It is important to ensure that the net charge of the lattice is zero to avoid an infinite energy sum, however this is not a concern when using the QEq method.

A class of performance optimisations to the Ewald method exist that depend on interpolating the atomic point charges onto a discretised grid or mesh [30]. Once the interpolation has been performed a fast Fourier transform algorithm can be applied to calculate the reciprocal space energy component, reducing computational time significantly. The implementation of a mesh based Fourier scheme was, however, beyond the scope of this research project.

An attempt was made to improve the performance of the classic Ewald through parallelisation of the long range evaluation which has a nested loop of depth 4. The 2 innermost loops were converted to run on the ‘compute unified device architecture’ (CUDA) processors included with recent Nvidia graphics cards. The ability to perform the operations within the 2 loops as a single vector process increased performance for that particular operation massively. In practice the overhead due to swapping memory between the graphics card and the processor generated enough time lag to negate any parallelisation performance boost, although when dealing with large system sizes the technique showed promise. The method although tested was not used for the calculations performed within this research project.

3.7 Lattice Relaxation

It is often necessary to relax a configuration of atoms to its minimum energy state after introducing some defect or strain. The primary relaxation method that was used extensively throughout this work is the conjugate gradient minimisation scheme. While theoretically the Fletcher-Reeves [34] conjugate gradient scheme is supposed to perform better when dealing with quadratic like functions, the Polak-Ribiere [78] method was found in practice to provide the quickest convergence to the minimum when used in conjunction with the ‘regula falsi’ line minimiser.

A caveat with the conjugate-gradient method, particularly when applied to configurations containing atoms at transition saddle points, is that on occasion a successively chosen conjugate direction could bring 2 atoms together such that the gradient exceeded numerically acceptable values and the minimisation would fail. On these occasions it was necessary to use a steepest descent method to
achieve rough convergence near the saddle point before letting the conjugate gradient method find the energy minimum more accurately.

3.8 Practical MD

The LBOMD package used in this thesis was written in Fortran 90 and run on a variety of architectures, in particular on an 8 core Intel Mac Pro under OS X 10.5. While the computational core of LBOMD was written in Fortran, in almost all cases external Perl scripts were used to generate input files and process the output files. Python was used to perform analysis on the output data using the NumPy and SciPy [72] with MatPlotLib generating many of the figures included in this thesis.

The modifications to the lattice input files to create interstitials, vacancies or ad-atoms were extremely laborious when manually editing the lattice files. A simple lattice editor was written using VPython and is shown in Figure 3.4 where an oxygen atom is being placed on the surface above a Ti atom. This editor was used extensively throughout this project and could be used to quickly delete, add and move atoms as well as allowing cropping of the lattice.

![Figure 3.4: The VPython lattice editor.](image)

While originally also useful for quick visualisation of a lattice configuration after running a simulation using LBOMD it was quickly supplanted in this respect by the ‘atomic visualisation and analysis’ (AVA) suite [82] developed by fellow PhD student Marc Robinson. Written in a mix of C and Python with bindings to the visualisation toolkit and the ability to render lattices using the POVray raytracing renderer, AVA was used to produce almost every lattice image included in this thesis.
Chapter 4

Saddle Point Methods

It is often the case that for a given lattice configuration it is quite straightforward to intuitively guess the binding sites of surface defects or valid interstitial sites, particularly when dealing with simple crystal structures and single species. For example the silver (1 0 0) surface using the Ackland [3] potential has a single unique binding site for an Ag ad-atom when symmetry is considered. If binding sites can be intuitively deduced it is a straightforward process to guess transitions pathways between neighbouring minima that are separated by only a single saddle point.

Having deduced a potential transition pathway it is often useful to calculate the associated energy barrier which can be used to ascertain the relative probabilities of various transitions and provide insight into various diffusion phenomenon as a function of temperature. Three barrier calculating methods have been implemented within this research project; the nudged elastic band (NEB) method [42] - used to calculate most of the barriers, the Dewar, Healy and Steward (DHS) method [23] used later in the project for performance purposes and the simple string method [26] which was used for rare transitions with interpolation issues.

As more complex potentials are implemented with multi-component materials it becomes harder to predict adjacent minima due to the potential for unintuitive configurations and the presence of metastable relaxation sites. Assuming we are interested in finding the evolution from a particular configuration it is necessary to use a potential energy surface exploration method to manually discover all the saddle points around a minima. Several similar algorithms exist to do this and the Dimer method [46], activation relaxation technique (ART) [62] and the, in-house developed, relaxation and translation (RAT) method have been implemented and are described in the following section.
4.1 Barrier Calculating

4.1.1 Nudged Elastic Band

Introduced by H. Jónsson et al. in 1998 [42] and improved upon by G. Henkelman on multiple occasions [47, 50] the NEB method is one of the most established barrier calculation techniques available. It is particularly useful compared to some methods as it provides both the transition barrier and minimum energy pathway (MEP) for a known transition.

Given an initial and final lattice configuration the NEB begins by linearly interpolating between those known states, providing a series of \( n \) evenly spaced images representing the intermediate configurations. We now have \( n \) points in 3N-dimensional space from which we can create \( n - 1 \) vectors joining each point to its neighbour, as shown in Figure 4.1.

![Figure 4.1: Schematic representation of 3 sequential images within the NEB.](image)

where \( \mathbf{R}_i \) is a point in 3N dimensional space representing the configuration of the \( i \)’th image, \( \mathbf{F}_i \) is the real force vector acting on the point \( \mathbf{R}_i \) and \( \mathbf{F}_{iP} \) and \( \mathbf{F}_{i\tau} \) are the parallel and perpendicular components of \( \mathbf{R}_i \) decomposed with respect to the tangent vector \( \mathbf{\tau} \).

The optimum tangent vector \( \mathbf{\tau} \) for an image \( i \) is dependent on the potential energy \( V_i \) relative to its neighbour and is given by [47]:
4.1. BARRIER CALCULATING

\[ \tau = \begin{cases} 
R_{i+1} - R_i & \text{if } V_{i-1} \leq V_i \leq V_{i+1}, \\
R_i - R_{i-1} & \text{if } V_{i-1} \geq V_i \geq V_{i+1}, \\
(R_{i+1} - R_i).V_{\text{max}} + (R_i - R_{i-1}).V_{\text{min}} & \text{if } V_i \leq V_{i-1} \leq V_{i+1}, \\
(R_{i+1} - R_i).V_{\text{min}} + (R_i - R_{i-1}).V_{\text{max}} & \text{if } V_i \leq V_{i+1} \leq V_{i-1},
\end{cases} \]  

(4.1)

where \( V_{\text{max}} \) and \( V_{\text{min}} \) refer to the maximum and minimum absolute energy difference between \( V_{i+1} \) and \( V_i \) and \( V_{i-1} \) and \( V_i \). Having removed the tangential component of real force \( F_{\tau} \) we introduce a spring force \( F_{iS} \) parallel to the tangent vector. The magnitude of the spring force scales with the separation of the sequential images, is dependant on a spring constant \( k \), and is given by

\[ F_{iS} = k \| (R_{i+1} - R_i) - (R_i - R_{i-1}) \| \tau. \]  

(4.2)

The total force acting on an image is then considered to be the sum of the spring force \( F_{iS} \) along the tangent vector and the perpendicular component of the real force \( F_{iP} \).

\[ F_i^{\text{new}} = F_{iS} + F_{iP}. \]  

(4.3)

The points are then translated into higher dimensional space such that \( n \) images in 3N space become a single point in 3Nn space allowing the images to be relaxed simultaneously which is crucial as the images are coupled. The images are iteratively relaxed using a conjugate gradient minimisation method with a ‘regula falsi’ line minimiser. Clearly the perpendicular component of force will allow the NEB to relax laterally downhill towards the MEP while the parallel spring force ensures that the images retain their spacing along the MEP.

An additional benefit of the NEB method is that it lends itself to parallelisation; the force acting on each image can be calculated in parallel. Throughout the course of this project a 10 image NEB has been used on an 8 core machine allowing each image to be simultaneously evaluated providing full parallelisation and a significant performance boost over the serial version.
4.1. BARRIER CALCULATING

Climbing NEB

Unfortunately whilst the NEB will converge on the MEP it is likely that the saddle point will lie between 2 successive images and thus either the barrier will be underestimated or some interpolation will be required introducing inaccuracy.

A refinement to the standard NEB is the climbing NEB [50] which modifies the force after several relaxation steps such that the highest energy image is allowed to move up the potential energy surface towards the saddle point.

\[
F_{i_{\text{max}}} = F_i - 2F_{1r}.
\]

(4.4)

Thus the spring force is ignored and the real force is reflected parallel to the tangent vector. Using this scheme the NEB is still able to relax onto the MEP whilst simultaneously converging the highest energy image onto the saddle point.

4.1.2 Dewar, Healy, and Stewart (DHS) Method

In an attempt to resolve issues when using the NEB with certain non-cooperative transitions and to provide greater computational efficiency, an alternative barrier calculating method was developed. Whilst this was independently conceived and implemented, in practice it is essentially the same as the DHS method developed by Dewar, Healy, and Stewart [23]. It is not surprising that the method was independently rediscovered as the underlying algorithm is simple and straightforward to implement. Unlike the NEB this method requires only 2 images to represent the initial and final configuration, however, it does not provide the MEP.

![DHS method](image)

Figure 4.2: DHS method. One end point is minimised with respect to the perpendicular force to the vector joining it to the other fixed point.
Having created 2 images in 3N space corresponding to the initial and final configurations the energy on each image is evaluated and the image with the lowest energy is translated along the linearly interpolated path towards the other end point.

The real force acting on the translated end point is decomposed into a perpendicular component of force, $F_T$, with respect to the interpolated vector between end points. The force is minimised as shown in Figure 4.2 using a conjugate gradient based rotational method to perform a constrained geometric optimisation such that the distance between the 2 images remains constant.

Once relaxed to within some tolerance the process of translation and relaxation is repeated for the lowest energy image until the images are within a user defined tolerance of each other, typically 0.01 Å. In the literature a small step-size is typically recommended, for example 0.2 Å [58] or 5% of the displacement vector [45], in order to avoid either of the end points crossing, and thus failing to bracket, the saddle point.

In practice it has been found it is more efficient to use an aggressive step-size such as 20% of the displacement vector. After each step the dot product of the force on each end point is calculated and if found to be positive it is clear that both points lie on the same side of the saddle and thus a crossing has occurred. Once a crossing has been detected the previous translation is reversed and the step percentage is halved with the convergence process repeated until the points have converged on the saddle or additional crossings have occurred. Whilst this inevitably results in wasted force evaluations the performance enhancements achieved by aggressively converging on the saddle compensate.

Despite the fact that the DHS algorithm is typically more efficient than the NEB, due to parallelisation a 10 point NEB can perform 8 force evaluations simultaneously and thus is often more attractive when manually determining a transition barrier. As the study evolved, certain situations arose where multiple barriers were calculated simultaneously and the DHS method became more useful.

4.1.3 String Method

The original string method [77] is an multi image interpolated transition barrier and MEP finding method much like the NEB. The justification for the development of the string method was to avoid the artificial penalty function that is introduced to the NEB in the form of a spring constant, eschewing spring forces for a periodic redistribution of the points along an interpolated pathway.
The core functionality of the string method is essentially the same as the NEB. For each image in the string a tangent vector following the MEP is calculated and the force acting on the image is then decomposed into parallel and perpendicular components. Having acquired the perpendicular force vector several minimisation steps are performed relaxing each image perpendicular to the string vector.

The primary differences between the NEB and the string method lie in the construction of the tangent vector at each string image; rather than using the linear displacement vectors as in the NEB method, cubic splines are constructed utilising the force and energy at each image and the tangent is taken as the vector perpendicular to the cubic spline at the image.

**Simple String Method**

For the purposes of this project a method was required to provide a transition barrier and an MEP for certain rare transitions that the NEB handled poorly and as such the string method seemed a sensible candidate. Unfortunately the original method proposed by Peters et al. [77] required rather complex implementation, however in 2007 E et al., proposed the ‘Simplified String Method’ which retained the reinterpolation of points along the string whilst removing all other features [27]. At each step each image is allowed to relax a small distance in the direction of real force; there is no decomposition of force into parallel and perpendicular components to the MEP. Of course the majority of the displacement vector will carry the image towards its respective minimum, however a small component will also bring it towards the MEP. In our implementation, a linear sequence of vectors are constructed joining each image and a redistribution of the images is performed such that they lie evenly spaced along the vector sequence; thus the component of force taking the image towards to the minima is compensated for whilst the component that moved the image towards the MEP is largely retained.

With a relatively large number of force evaluations, up to twice that of the NEB, the string will converge to the MEP and provide a transition barrier with reasonable accuracy. It is also possible to use the climbing image technique to converge on the barrier with greater accuracy using a weighted average of displacement vectors as used in the NEB.

In practice the simple string method was extremely straightforward to implement and performed better than expected, providing transition information within a reasonable timeframe and even
outperforming the NEB in cases where transition pathways are non-monotonic in 3N Euclidean space.

4.1.4 Benchmarking

Whilst the NEB was used for the majority of barrier calculations shown in this work, the DHS method was used for later parts of the project where large numbers of barrier calculations needed to be performed in parallel and the string method was used in rare cases where the NEB failed. To provide some insight into the relative performance characteristics of the NEB, DHS and string method, the barriers for a simple, oxygen ad-atom hop and complex transition involving a TiO$_2$ unit rotating over an oxygen ad-row on the rutile TiO$_2$ surface have been calculated to within 0.001 eV and the number of relative force evaluations compared.

<table>
<thead>
<tr>
<th>Barrier Type</th>
<th>NEB</th>
<th>DHS</th>
<th>String</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Ad-atom Hop</td>
<td>682</td>
<td>584</td>
<td>978</td>
</tr>
<tr>
<td>TiO$_2$ Rolls Over Oxygen Ad-row</td>
<td>3282</td>
<td>1697</td>
<td>2736</td>
</tr>
</tbody>
</table>

Table 4.1: A comparison of the NEB, DHS and simple string transition finding algorithms applied to both a simple and complex transition.

As can be seen in Table 4.1 the DHS method gives considerable performance benefit where complex non-monotonic transitions are concerned, however the NEB is often more useful in practice due to its parallelisation, rendering the NEB 4.14 times faster than the DHS method even when considering the complex transition. Later when processor power becomes more of a restraint the DHS becomes useful. The string method offers a marginal advantage over the NEB when looking at a complex transition, however, the real use of the string method was in cases where the NEB would fail to converge at all.

4.2 Saddle Point Finding

The second class of barrier methods are those that are able to converge on a saddle point without any prior knowledge of the corresponding transition. While it is often possible to intuit a series of transitions that will allow, for example, defect diffusion, in many cases it is dangerous to make assumptions regarding the behaviour of the potential energy surface. Often it is the case that novel and complex transitions provide the lowest energy diffusion barriers for a lattice configuration.
A good example of unexpected behaviour providing a low diffusion barrier is the diffusion of an Al ad-atom on the Al (110) surface; Henkelman found [46] the lowest energy diffusion mechanism requires an exchange with a neighbouring surface atom rather than a direct hop. Whilst a simple nearest neighbour exchange would have been tested using a barrier calculating method such as the NEB it is very unlikely the 3rd lowest energy diffusion mechanism would have been conceived, involving a 3 neighbour knock on exchange mechanism.

The Dimer method, ‘activation and relaxation technique’ (ART) and ‘relaxation and translation’ method (RAT) are the three saddle-point finding mechanisms that have been implemented during the course of this research project. All 3 methods rely on the principle of finding and following the ‘mode of minimum curvature’; if a point lies on the MEP, calculating the Hessian matrix at that point along with its corresponding eigenvalues and eigenvectors will yield the vector parallel to the MEP at that point, in the form of the eigenvector with the lowest corresponding negative eigenvalue. Whilst repeatedly calculating the Hessian matrix would allow quick convergence on the saddle point, in practice the evaluation of the Hessian matrix is too computationally expensive. The 3 methods used allow estimation of the modes of minimum curvature without having to evaluate the Hessian matrix.

### 4.2.1 Search Initialisation

All three transition search methods have in common the means by which the search is initialised and as such this warrants separate discussion. The fundamental principle behind the initialisation of the search is the offset of the lattice configuration from minimum energy by some random displacement vector.

The construction of the displacement vector is an initial point of interest. Henkelman and Jönsson [46] suggest displacing each free coordinate according to a Gaussian probability distribution of width 0.1 Å. For this research project a simple vector of length 3N with each element containing a randomly generated number between -1 and 1, normalised and multiplied by a desired step-size, has found to allow convergence on the full range of saddle points when testing on silver and TiO$_2$. While initially a fixed step-size between 0.1 and 0.4 Å was used, a randomised step between 0.1 and 0.5 Å has been found to provide the quickest convergence on multiple saddle points.
4.2.2 Limiting Configuration Space

Unfortunately both displacement methods scale poorly with system size; as the number of coordinates in configuration space increases so do the number of potential saddle points available from the initial configuration. It is possible, however, to artificially limit the configuration space, allowing only coordinates of interest to remain free. Considering an Al ad-atom resting on the (1 1 0) surface of a perfect lattice; the lowest energy transitions will be those that involve the Al ad-atom. A simple improvement would be to fix all atoms that are beyond some cut-off radius from the defect of interest thereby restricting configuration space. Of course fixing too many atoms would artificially limit the number of saddle points available; Henkelman and Jónsson [48] investigated this effect and found that using fewer than 20 free atoms surrounding an ad-atom on a 300 atom substrate would remove many exchange mechanism based saddle points from the search space for the Al ad-atom.

The scheme used in this research project, was developed by Stewart Gordon [39], and resolves the scaling problem slightly differently. Fixing too many atoms artificially limits the number of saddle points available from a minimum configuration primarily because the external atoms are unable to relax during the search process. It is crucial to recognise the difference between driven movement, i.e. the atoms are moved uphill by the transition search and may well end up in a new configuration after relaxation of the lattice, and passive movement where the atoms are required to relax or ‘breathe’ in order to allow a transition to occur, the method used in this research project takes advantage of this distinction.

A ‘search’ array is created containing indices to all atoms that remain close enough to the defect to be of interest and hence are driven in the transition search. As the search method is executed the force acting on all atoms outside of the search array is closely monitored and if found to exceed some threshold all atoms within the search array are frozen and all atoms outside of the array are allowed to relax. This allows us to reduce the search array and hence configuration space to lower than would be acceptable when simply fixing external atoms, thereby increasing performance. It is necessary to compensate for potential drift of periodic lattices, where absolute comparison of atomic positions would produce large numbers of anomalous defects. A straightforward mechanism to compensate for drift is to calculate the average displacement vector for all atoms and if above some threshold, subtract the average displacement vector from each unique atomic displacement vector.
4.2.3 The Dimer method

The dimer method \cite{46} is one of the most well established saddle point finding mechanism. Developed by Henkelman and Jönsson, the dimer method is called such as it relies on an abstract dimer representing 2 points in 3N configuration space, as shown in Figure 4.3, offset by some small distance.

Figure 4.3: The dimer method: The real force acting on each end of the dimer is decomposed into parallel and perpendicular components, \( F_P \) and \( F_T \)

Using \( R \) to describe our point in 3N dimensional space, the first step of the dimer method is to offset \( R \) along some randomised displacement vector, \( \hat{N} \), as described previously. The 2 end points of the dimer, \( R_1 \) and \( R_2 \) are then created by diametrically displacing a small distance, \( \Delta R \) along \( \hat{N} \) such that \( R_1 = R - \Delta R \hat{N} \) and \( R_2 = R + \Delta R \hat{N} \). Henkelman and Jönsson recommend \( \Delta R \) of \( 1 \times 10^{-3} \) Å however we found larger diametric displacements produced improved results with some potential surfaces.

Rotational Minimisation

The dimer acts to find the lowest curvature mode through minimising the rotational force acting on the dimer. This is achieved through decomposing the force acting on each point into parallel and perpendicular components, \( F_{IP} \) and \( F_{IT} \) respectively. The global rotational force acting on the dimer is then given by:

\[
F_T = F_{2T} - F_{1T}
\]
and the decomposition of force into a perpendicular component is readily achieved by subtracting the parallel component:

\[ \mathbf{F}_{\text{PT}} = \mathbf{F}_1 - (\mathbf{F}_1 \cdot \mathbf{N})\mathbf{N} \]

while the real force acting on the dimer is taken to be the sum of the individual forces:

\[ \mathbf{F} = \mathbf{F}_1 + \mathbf{F}_2. \quad (4.5) \]

The dimer energy, \( E = E_1 + E_2 \), is minimised by minimising the global rotational force, \( \mathbf{F}_\text{T} \). The minimisation process consists of 2 components; a conjugate gradient mechanism which selects planes of rotational minimisation, along with the rotational equivalent of a line minimiser. The conjugate gradient scheme is the same as described previously, however the rotational line minimiser is of great importance as it strongly effects the overall efficiency of the algorithm.

Figure 4.4: Rotation of the dimer: A trial rotation \( d\theta \) is used to calculate a minimisation step, \( \Delta \theta \)

Figure 4.4 introduces the notation for describing the rotational minimisation. As previously described the conjugate gradient method is used to select successive planes of minimisation and this plane is defined by the orthonormal vectors \( \Theta \) and \( \hat{\mathbf{N}} \). For the first rotational minimisation \( \Theta \) is
parallel to the rotational force acting on the dimer, $F_T$. After a trial rotation $d\theta$, which can be $10^{-4}$ radians or greater, a modified perpendicular vector, $\Theta^*$ is produced along with corresponding modified forces $F^*$ and $F_T^*$.

The aim of the rotational minimiser is to reduce the component of rotational force acting within the plane to zero and this scalar force is quantified as, $F$:

$$F = F_T \cdot \Theta / \Delta R$$

and a finite difference approximation of the change in rotational force is given by:

$$F' = \frac{dF}{d\theta} \approx \frac{F^* \cdot \Theta^* - F \cdot \Theta}{d\theta}.$$ 

**Modified Newton Method**  The first rotational minimisation scheme proposed by Henkelman and Jönsson is a modified Newton method and is simply given by:

$$\Delta \theta \approx \frac{F^* \cdot \Theta^* + F \cdot \Theta}{-2F'}$$

however they found this method tended to overshoot the minimum.

**Harmonic Approximation**  Next they tried a sinusoidal fit to describe the energy of the dimer as a function of rotation. They found the rotational force acting on the dimer could be approximated by:

$$F(\theta) = A \sin 2(\theta - \theta_0)$$  \hspace{1cm} (4.6)

where $\theta_0$ is the angle required to minimise the rotational force within the plane. Therefore $F'$ is given by the derivative of the function:

$$F'(\theta) = 2A \cos 2(\theta - \theta_0).$$  \hspace{1cm} (4.7)

We can reduce Equations 4.6 and 4.7 to one expression:

$$\frac{F}{F^*} = \frac{1}{2} \tan(-2\theta_0)$$
which when inverted yields the rotation required to minimise force, $\theta_0$:

$$\Delta \theta \approx \theta_0 = -\frac{1}{2} \arctan\left(\frac{2F}{F'}\right)^{-1}.$$

‘Regula Falsi’ Estimation  Unfortunately even the sinusoidal approximation was found to be inefficient in many cases and we discovered that the ‘regula falsi’ interpolation [35] of the force resulted in the quickest convergence on the local minima.

Assuming 2 trial rotations, $A$ and $B$, have been performed, the rotation required to minimise the function is:

$$\Delta \theta \approx \frac{F'(A)B - F'(B)A}{F'(A) - F'(B)}.$$

This was first used to bracket the minima by deliberately over estimating $\Delta \theta$ through simply scaling by 1.5. Once bracketed the algorithm quickly converged on the saddle point, consistently outperforming the previous 2 methods, requiring typically 4 or 5 force evaluations to minimise the rotational force within the plane.

Translation

The translation of the dimer is relatively simple compared to the rotational minimisation. 2 translational schemes are used, the first allowing the dimer to aggressively travel out of regions of positive curvature, while the latter allows accurate convergence on the saddle. Thus a means of calculating the curvature of the potential surface along the dimer vector is required:

$$C = \frac{(F_2 - F_1) \cdot \hat{N}}{2\Delta R}.$$

If we are in the neighbourhood of a minimum, the force acting on $R_2$ along $N$ will be greater than that at $R_1$ and hence the curvature will be positive, whilst closer to the saddle point the opposite will be true. The 2 schemes for translating the dimer are as follows:

$$F_{\text{mod}} = \begin{cases} F_P & \text{if } C > 0, \\ F - 2F_P & \text{if } C \leq 0, \end{cases} \quad (4.8)$$
where $F_P$ is the component of force parallel to the dimer vector and is given by: $F_P = (F \cdot \hat{N})N$ and $F$ is the real force acting on the dimer given earlier in Equation 4.5.

In order to optimise the efficiency of the algorithm it is sensible to move away from a fixed step size by making the step a function of the potential energy surface. The method used is common to all three saddle point search algorithms and is described in Section 4.2.6.

**Application of the Methods to P.E. Surfaces**

It is difficult to understand the behaviour of potential surface algorithms like those included in this chapter due to the high dimensionality of configuration space. In order to provide some visual feedback on the behaviour of the dimer method, a 2D eggbox was created which allowed the dimer to perform searches on a variety of 2D potential functions. A simple potential surface that provided curved minimum energy pathways was the following distorted eggbox shown in Equation 4.9 and is shown in Figure 4.5

$$E = \sin(x - \frac{y^2}{40}) + \sin(y - \frac{x^2}{20})$$  \hspace{1cm} (4.9)

![Figure 4.5: The 2D eggbox potential creating using Equation 4.9.](image)
A dimer search was initialised from the minimum at (-1.5, -1.5) by offsetting through a displacement vector of magnitude 0.2 along the direction [-1, 0.5]. Figure 4.6 demonstrates the dimer evolutions during a typical search. The colour change from red to blue represents the transition from regions of positive to negative curvature. The yellow line demonstrates the real force $F$ acting on the dimer while the green line shows the direction of modified force $F_{\text{mod}}$ and hence the translation direction, the step size is fixed at 0.3.

![Figure 4.6: Dimer search on a distorted eggbox potential.](image)

Figure 4.6 demonstrates the dimer algorithm quite clearly; in regions of positive curvature the inverted component of force parallel to the dimer vector is used to translate the dimer and hence it travels along the dimer vector, $N$. Once in a region of negative curvature the component of force parallel to the dimer is flipped and hence it is able to relax laterally whilst still climbing towards the saddle. Obviously due to the large translation step the dimer does not converge perfectly on the saddle, a smaller step-size would compensate for this.
4.2. Activation Relaxation Technique

The dimer method performs excellently when using simple 2D potential functions and when using some complex many-body empirical potentials such as the Ackland EAM silver potential which was also tested as part of this research project. Unfortunately some potential functions have extremely ‘choppy’ potential surfaces which the dimer method is sensitive to; this appears to be particularly bad in the case of ionic systems using the QE$\text{q}$ scheme. These noisy potential surfaces have many metastable sites with extremely small escape barriers that nonetheless confuse the dimer algorithm by quickly alternating between regions of positive and negative curvature. When performing dimer searches on these surfaces the dimer will eventually converge on a saddle point, however it is common to find that the dimer has become trapped in a region where the primary component of $\mathbf{F}_{\text{mod}}$ points towards the previous location of the dimer, while only a small component translates the dimer towards the saddle point, thus requiring an unacceptably large number of force evaluations before converging.

In order to locate saddle points on these noisy potential surfaces a more coarse method of traversing the potential surface was required, something the activation relaxation technique (ART) provided. Developed by Barkema and Mousseau [7] in 1998 it is unsurprising that the ART precedes the dimer method as it is fundamentally very simple. By activation and relaxation Mousseau and Barkema are describing the 2 steps required when finding saddles and their corresponding barriers; activation - driving the system from a local minimum to a neighbouring saddle point and relaxation - relaxing from the saddle point into a corresponding neighbouring minimum. Obviously it is the ‘activation’ part that is challenging and which the ART aims to resolve.

Unlike the dimer method the algorithm relies on an single point in 3N space traversing the potential energy landscape. At each step of the ART a vector, $\mathbf{N}$, is constructed that tethers the displaced point $\mathbf{R}$ to the origin $\mathbf{R}_0$. Much like the the dimer method, the forces acting on $\mathbf{R}$ are decomposed into parallel and perpendicular components with respect to $\mathbf{N}$, as shown in Figure 4.7.
The fundamental assumption of the ART is that transition MEPs generally move away from their respective minima. If this assumption holds true then a perpendicular relaxation of a point \( R \) with respect to the displacement vector \( N \) will allow the point to travel towards the MEP without relaxing towards the local minima.

After displacing the point \( R \) from the origin \( R_0 \) using the means described previously a modified force, \( F_{\text{mod}} \), acting on the point is constructed:

\[
F_{\text{mod}} = F_T - \alpha \cdot F_P.
\]

Here \( \alpha \) is a scalar variable that controls the aggressiveness of the algorithm. A large value of \( \alpha \) will allow the point to climb rapidly away from the minimum relative to the lateral minimisation, however the convergence on the saddle point may be poor or the saddle point missed altogether. A smaller value of alpha allows the lateral minimisation towards the MEP to dominate the saddle point search and hence may provide excellent convergence with poor efficiency. Mousseau and Barkema suggest a value for \( \alpha \) of \( 0.15/|R - R_0| \).

**Modified ART**

The form of the ART method implemented for this research differed slightly from the original form. Whilst the direct implementation of the method was successful in converging on multiple saddle points it was recognised that the component of lateral minimisation \( F_T \) was not being used as efficiently as
4.2. SADDLE POINT FINDING

possible. By de-coupling the lateral minimisation towards the MEP from the translation towards the saddle, much greater efficiency was achieved.

Rather than use the $\alpha$ parameter to ensure reasonable convergence on an MEP, the force $F_T$ acting perpendicular to point $R$’s displacement vector was monitored and if found to exceed a tolerance was minimised. During the course of implementing the dimer method an efficient rotational minimiser was developed and this was applied to the lateral relaxation of the forces acting on $R$ with respect to its displacement vector $N$.

Translation

The translation of the search point $R$ is extremely straightforward. In the original form of the ART the modified force direction is used to translate, i.e. the force vector is normalised and multiplied by some scalar value, the determination of which is described in Section 4.2.6, and added to our search position such that $R = R + |F_{\text{mod}}| \times \text{Step}$.

When using the modified ART method the translation step becomes even more simple; as the lateral rotational has been minimised, $F_T$ is effectively zeroed and hence the point, $R$, is translated uphill along the displacement vector from the origin, $N$.

Non-Monotonic and Highly Curved Transition Pathways

An inherent issue with the previously stated ART is the reliance on linear MEPs that are not highly curved, the assumption being that the MEP between 2 minima will never have a component that is perpendicular to the linear vector joining each minima. In practice this is a very safe assumption however there are still cases where the ART performs poorly because the energy pathway is far from linear. Barkema and Mousseau address this issue by suggesting the use of a trail of previously visited points behind the search point, $R$. Rather than tether our exploration point $R$ to the origin $R_0$ the trailing points are used to provide a constantly updated displacement vector, where the tether point is the first point in the historical trail that is greater than $r_T$ distance away from $R$.

Implementation of a trailing tether met with mixed success; in some cases the convergence on the saddle would take fewer function evaluations, whilst in others the search would turn such that the perpendicular component of minimisation allowed the search point $R$ to relax back towards the original minimum and thus the search failed. Whilst the use of historical position data was not
effective for the ART method, the idea is revisited with the RAT method in the following section.

2D Eggbox

The ART method was also implemented in a form that could be applied to a 2D eggbox potential. Figure 4.8 demonstrates the ART method initialised in the same fashion as the previous dimer example, a displacement of 0.2 in the [-1, 0.5] direction from (-1.5, -1.5).

Figure 4.8: ART search on distorted eggbox potential

The parameters used were: \( \alpha = 0.6/|R - R_0| \) with a fixed translation step-size of 0.1. The kink in the line near the saddle-point is easy to understand; the component of the translation step that carries the point uphill towards the saddle point is determined by the parallel component of force to the displacement vector. As the search approaches the saddle point the component of force parallel to the displacement vector tends to zero, hence the translation direction becomes dominated by the lateral forces and the point zigzags. \( \alpha \) must be carefully chosen to avoid this, with the best choice of \( \alpha \) being dependent on the potential surface you are working with. A low \( \alpha \) prefactor will zigzag a large amount as shown in Figure 4.9(a), thus requiring a large amount of function evaluations before converging on the saddle.

Using a high \( \alpha \) prefactor avoids kinks in the search path, however coarsens the result such that the saddle point can be missed entirely as shown in Figure 4.9(b). An \( \alpha \) prefactor of 0.6 was found to provide the best efficiency to accuracy ratio.

Mousseau and Barkema recognised this feature with the ART and have made multiple revisions of the technique to alter the behaviour of the search once in the neighbourhood of a saddle point [14],
4.2. SADDLE POINT FINDING

4.2.5 Relaxation and Translation Method

The primary issue with the ART is a strong bias towards finding the same saddle points multiple times; a large number of transition searches were required before we could have any confidence that the full set of low energy transitions had been found. This was at least partially due to the constraint of transition linearity, with nicely behaving linear transitions dominating the results of the ART search algorithm.

The RAT method borrows much of the principle behind the ART whilst having no bias related to transition linearity. Much like the ART the RAT method relies on decomposition of forces into parallel and perpendicular components, $F_P$ and $F_T$ respectively, using a tether point to construct the vector that allows force decomposition. As with the proposed improvement of the ART suggested by Mousseau and Barkema, the tether is allowed to move with the search point, however in this case the point $R_i$ is tethered to the previous historical step $R_{i-1}$. For the first displacement the decomposition of forces is identical to that of the ART, where this technique differs is how the lateral forces are minimised.
Force Minimisation

In this method the search point, \( R \) is allowed to travel within the plane bound by the span of perpendicular vectors to the tether vector, \( N \). While \( R \) is moved to relax the component of force perpendicular to \( N \), \( N \) itself is not re-adjusted to sustain the tether, as shown in Figure 4.10. Where this method differs from the ART and the dimer method is that it is quite possible and even likely that the search point will move a large distance during the relaxation stage of the algorithm.

![Figure 4.10: RAT method: The point R is relaxed within the plane bound by the span of perpendicular vectors to N.](image)

As the relaxation stage can require large movements within the plane, it was important to develop an algorithm to dynamically alter the size of the relaxation step in order to improve efficiency. Originally the ‘regula falsi’ line minimiser described previously was trialled, however in many cases the curvature in the direction of the line minimisation was found to be positive and thus the estimation was poor. A simple algorithm that looks at the relative change in force between steps was found to provide reasonable efficiency:

If \( \frac{F_T - F_{T_{i-1}}}{F_T} < 0.2 \), then scale the step size by 1.2, otherwise reduce by a factor of 2.

Therefore, if the change in force during a minimisation step is less than 20% of the force at the current step, the relaxation step needs to be more aggressive, while if the change in force was
4.2 SADDLE POINT FINDING

greater than 20% the relaxation step must decrease to ensure accurate convergence on the minima. Despite being a relatively crude algorithm it allowed for reasonable efficiency with $\sim 4$ force evaluations required per plane minimisation.

Translation

Whilst the RAT method uses a trailing historical point in order to decompose forces acting on the current search vector it differs from the ART in that it also stores and utilises the historical displacement vector.

As shown in Figure 4.10, after each relaxation step there are a pair of vectors $\mathbf{N}$ and $\mathbf{N}'$ that define the initial displacement of the search point and the final relaxation point respectively. Given these 2 displacement vectors the new translation direction vector is easily constructed:

$$\mathbf{N}_{i+1} = \frac{\mathbf{N}_i + \mathbf{N}'_i}{|\mathbf{N}_i + \mathbf{N}'_i|}. \quad (4.11)$$

As $\mathbf{N}_{i+1}$ is clearly normalised, it is obvious that $\mathbf{N}_i$ is a vector of unit length whilst $\mathbf{N}'_i$ is not. This distinction between the vectors is important, failure to ensure that the new direction is weighted by the magnitude of the relaxed $\mathbf{N}'$ vector results in searches looping towards the origin as seen with the moving tether when using the ART.

2D Eggbox

As with the dimer and the ART, the RAT method was tested using the distorted 2D eggbox, initialised from (-1.5, -1.5) and displaced by 0.2 in the (-1, 0.5) direction. Figure 4.11 shows the results for the RAT method using a fixed step-size of 0.2.
The component stages of minimisation within the plane and translation are clearly visible. By using a distinct translation and minimisation step the algorithm could be quite inefficient, however excellent convergence on the saddle is achieved with a relatively low number of function evaluations.

### 4.2.6 Translation Step-Size and Saddle Point and Minima Detection

Several algorithms are common for all methods and therefore are given in this section.

**Translation Step-Size** The method for determining step-size is simple and relies on recording the current and previous translation vectors, $\mathbf{N}_i$ and $\mathbf{N}_{i-1}$. If the potential energy surface is well behaved in the region of the search point, it would be expected that several successive search iterations would move the search point in a similar direction. By examining the curvature of the transition search path we can judge whether it is appropriate to increase or decrease the translation step:

If $\mathbf{N}_i \cdot \mathbf{N}_{i-1} > 0.8$, then scale the step-size by 1.5, otherwise reduce by a factor of 2.

Obviously limits are placed on the maximum and minimum step-size to avoid runaway problems. Whilst simple, this algorithm succeeds in accelerating the search point along well behaved regions whilst decelerating when strong curvature is experienced, such as in the region of a saddle point.
Saddle Point Detection  While the search algorithm is running, how can we have confidence that a saddle point has been crossed? One method is to record the force acting on the search point; as it crosses the saddle point along the MEP the force should in theory invert to push the search point towards the new minimum. In practice this algorithm quickly falls apart; as the point approaches the saddle the lateral forces become comparable to the force parallel to the MEP, as such it is quite likely that a saddle point will be detected due to rattling either side of the MEP prior to actually crossing the saddle.

The most consistently effective detection method is to simply monitor the component of force acting on the search point that is parallel to the displacement vector from the origin, as shown in Figure 4.12

![Figure 4.12: The component of force parallel to the displacement vector inverts as the search point crosses the saddle.](image)

By utilising the displacement vector \( \mathbf{N} \) and the real force currently acting on the search point, \( \mathbf{F}_i \) it is simple to check if the point has crossed the saddle by calculating if \( \mathbf{F}_i \cdot \mathbf{N} > 0 \). Whilst this method was used to good effect in this research project, it cannot be guaranteed that the condition will be immediately true after crossing the saddle.

Minima Detection  The detection of minima during a line minimisation warrants mention here purely because it is the inverse of the saddle point detection method. If \( \mathbf{F}_i \cdot \mathbf{N} < 0 \) where \( \mathbf{N} \) is the displacement along the minimisation direction, then we have crossed the minimum and the minimisation is terminated.

4.3 Benchmarking

The previous sections provided some insight into the implementation and behaviour of the 3 transition search methods implemented as part of this research project. Using the 2-dimensional implementations
of the transition algorithms demonstrated previously it was possible to provide a more thorough comparative analysis.

\[ E = \sin(x - \frac{y^2}{X_{\text{dist}}}) + \sin(y - \frac{x^2}{Y_{\text{dist}}}) \]  

(4.12)

Equation 4.12 is similar to the distorted eggbox potential surface demonstrated earlier and was used as a foundation for the investigation into the relative performance. 1000 searches were performed using each transition finding algorithm. At the beginning of each search a random value of \(X_{\text{dist}}\) and \(Y_{\text{dist}}\) was generated between -100 and 100 inclusive taking care to discard 0 values. For each search the number of function evaluations required was recorded, however, if the number of function calls exceeded 200 using the RAT or ART methods, or 100 using the dimer method the search was considered to have failed. The differentiation between the number of function evaluations permitted for the ART and RAT versus the dimer method was due to the fact that the dimer method requires 2 force evaluations at every step.

Through randomising the 2D eggbox, the valid minima from which to initialise searches is moved. As such it was necessary to perform a steepest descent minimisation initiated from (-2, -2) for each new configuration. In order to determine the appropriate parameters for the 3 techniques, optimisation was performed such that they all converged to within 1% of the saddle point energy of the non-distorted eggbox. This equated to the following parameters:

- **Dimer**: Translation step-size: 0.2
- **ART**: Translation step-size: 0.1 - Alpha prefactor: 1
- **RAT**: Translation step-size: 0.2 - Relaxation step-size: 0.1

An additional approximation was made for the dimer method. Ideally an optimised rotational minimiser is used to reduce the number of function evaluations required, however the version employed within the 2-dimensional code was not optimal, requiring more evaluations then would have been ideal. In order to compensate for this it was assumed that each rotational minimisation step required just 2 function evaluations to fully minimise curvature; this is a generous assumption and it is possible an efficient rotational minimiser would require more on average.

While each transition search algorithm was started within the minimum found using the steepest descent search, the starting point was translated 0.2 along a randomly generated displacement vector.
before the search was initiated.

<table>
<thead>
<tr>
<th></th>
<th>Av. Function Evaluations</th>
<th>Convergence Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer</td>
<td>38.4</td>
<td>96.5</td>
</tr>
<tr>
<td>ART</td>
<td>39.5</td>
<td>97.7</td>
</tr>
<tr>
<td>RAT</td>
<td>36.6</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4.2: Benchmarking the Dimer, ART and RAT searching a 2-D distorted eggbox.

Table 4.2 demonstrates that average number of function evaluations required between methods are relatively close with less than 8% deviation between all 3 results. The ART and dimer methods are particularly close, however the 2D potential surfaces are ideal for the ART method due to the monotonic minimum energy pathways and as such it is possible that in practice when dealing with 3N dimensional surfaces the dimer method will outperform the RAT method. More significant is the fact that while the performance is similar, both the dimer and ART fail to converge within the maximum permitted number of function evaluations on several occasions. In many cases where the dimer failed to converge, it arrived within the region of the saddle point and it would oscillate in the vicinity, approaching the saddle point however requiring excessive function evaluations and hence failing. This suggests that the failure rate of the dimer method could have been improved had some additional translational scheme been employed in the direct neighbourhood of the saddle point. Figure 4.13 is an example of one such failed search, the proximity to the saddle point is demonstrated by the green RAT pathway. The dimer method appeared to be particularly hampered when converging on saddle points with high positive curvature.
While the dimer method would typically fail through exceeding the maximum number of function evaluations while approaching the saddle, the ART method would often fail due to missing the saddle point entirely and moving into a neighbouring minimum, despite having a moderate $\alpha$ prefactor as shown in Figure 4.14.

The ART method performs poorly when initially orientated towards adjacent maxima as the
component of force perpendicular to the displacement vector is small, thus the ART point turns slowly.

4.3.1 Conclusions

All three methods perform well and are able to converge on the full set of available saddle points with a high success rate. The dimer and RAT methods are particularly successful with convergence on or near the saddle point in almost all cases, with the dimer suffering from performance rather then convergence issues. The ART method works well when orientated in the general direction of the MEP and therefore achieved a higher success rate then the dimer method although of the three techniques it is the only one that has the potential to completely miss the saddle point. The RAT method performs excellently achieving a perfect success rate and the greatest average efficiency.

The behaviour seen here translates well to that seen when using the 3 techniques to perform transition searches with real molecular systems. The ART method performs well with monotonic transitions such as simple hops, while failing often and requiring many searches to find the full set of available transitions for more complex configurations. The dimer performs well and is able to obtain the full set of available transitions for almost all configurations, however suffers from severe convergence issues and as such is computationally expensive. The RAT method performs the best of the 3 techniques and is able to rapidly converge on simple monotonic transitions pathways like the ART method whilst obtaining the full set of transitions for any given configuration. An additional benefit of the RAT method is a bias towards resolving lower energy transitions, something not seen using the dimer method.

Four random successful searches out of the 1000 performed are shown in Figure 4.15 to demonstrate the various characteristics of the 3 methods.
Figure 4.15: 4 randomly chosen sets of transition searches. The green line is the RAT method, blue the ART method and the dots indicate the dimer pathway.
Chapter 5

Long Time-Scale Dynamics

It was described in the introduction that due to computational limitations it is necessary to wisely choose our modelling methodology in order to achieve the desired time and/or length scales. Figure 1.1, shown in the introduction, outlines the domains for which various simulation methodologies are generally appropriate. When modelling sputtered growth using empirical potentials it is likely that the deposition rate for the system size being considered will be on a time-scale inaccessible using classic MD and as such even the longest practical MD simulations would not be able to reproduce multilayer growth. The simplest way to compensate for this time differential is to artificially increase the deposition rate such that it occurs within the MD time-frame. However, with simulated depositions occurring with a frequency many orders of magnitude greater than in the realistic process it is likely that the modelled growth dynamics will be biased, with slow diffusion processes not having time to occur between subsequent depositions. A relatively simple technique to allow less frequent events to experience an acceleration proportional to the increase in deposition rate is through artificially scaling the temperature of the simulation. However, this biases dynamics as the relative change in attempt frequency for all transitions is non-linear.

There are a class of techniques that utilise harmonic transition state theory [32] in order to increase the time-evolution of the simulations without biasing the dynamics: Long time-scale dynamics methods. Of these methods the kinetic Monte Carlo and adaptive/on-the-fly KMC are described due to their application within this research project.
5.1 Kinetic Monte Carlo

The kinetic Monte Carlo (KMC) method, when applied to MD, exploits the symmetry of the simulation due to the crystallinity of what is being modelled. Consider a simple defect such as a Cu ad-atom on a Cu FCC (110) surface; the simplest diffusion processes are extremely simple to predict and involve the ad-atom making the direct hop into the neighbouring and symmetrically equivalent sites. However, despite the relative simplicity of the problem if the temperature of interest is low and the diffusion barriers are sufficiently high, modelling the diffusion behaviour of the ad-atom will be impossible as the ad-atom will be trapped vibrating within its current potential well for the majority of the simulation.

When dealing with simple diffusion processes within crystal structures it is possible to translate MD simulations onto a rigid array of discrete points, with each point representing a potential energy minimum for an atom. This discrete array can be 2-dimensional such as in the case of the Cu ad-atom diffusion, or can be 3-dimensional when considering the evolution of vacancies and interstitials within a bulk material. An example of the translation of real molecular dynamics behaviour onto a discrete array is demonstrated in Figure 5.1 which shows the 2-dimensional evolution of the Cu ad-atom.

![Diagram of Cu ad-atom diffusion](image)

Figure 5.1: The left hand side shows the evolution of a Cu ad-atom on the (110) surface while the right hand shows the discretised KMC equivalent. Adapted from [33].

Defect diffusion is a well understood probabilistic process and is a function of the lattice temperature, the set of barriers that allow a defect to escape from a given configuration and the prefactors associated with each transition. Through the translation of the defect diffusion onto a discretised
array it becomes possible to avoid the MD simulation entirely and to recreate realistic stochastic
behaviour using the Arrhenius equation:

\[ \text{Escape frequency} = \nu e^{-E_b/k_B T} \]

where \( E_b \) is the transition barrier, \( k_B \) is the Boltzmann constant, \( T \) is the temperature in Kelvin and \( \nu \) is the transition prefactor.

The evolution of the KMC is considered to be a Markov process as the transitions from any given
configuration are independent of the previous system evolution and time. As the KMC evolves the
configuration between equilibrium configurations, the algorithm is said to show detailed balance [57],
however unlike the original Metropolis Monte Carlo algorithm [65], the KMC method is not ergodic.

**Vineyard’s Prefactor** Vineyard [101], using harmonic transition state theory [32], determined
that the prefactor would be given by the ratio of the products of the positive vibrational frequencies
of normal modes at both the transition minimum and the saddle-point. This requires that the lattice
configuration at the saddle point is captured accurately either using the DHS method, or the climbing
image combined with the NEB or string methods.

For the purposes of this research project a program that calculated prefactors was written in
a combination of Perl and Fortran. The Hessian matrices at the saddle point and minimum were
calculated numerically to allow for portability and to avoid complex analytical derivatives. The high
performance Lapack (Linear Algebra PACKage) library was used [5] in order to rapidly calculate
the eigenvalues from large Hessian matrices. In order to improve efficiency a limited subset of all
atoms were included when numerically calculating the matrix of mixed second derivatives. It seems
reasonable that atoms that undergo little movement when translating from the minimum to the
saddle-point are effectively unperturbed by the transition and thus will produce highly similar and
therefore cancelling eigenvalues. The code was written such that once the user specified a desired
number of included atoms a binary search was performed to ascertain the minimum translation
distance to provide the correct number of atoms. It is worth noting at this point that original
implementation of the Vineyard prefactor calculation included atoms based on their proximity to the
primary transition atom. This resulted in poor convergence, with large numbers of atoms required
before a useful result could be acquired. Additionally due to the large radius required, there were
issues with boundary collisions and overlap with fixed atoms. Once atomic displacement was used as the determining factor for inclusion in the Hessian matrix it was found that convergence could be achieved typically using less than 1000 atoms. While the Vineyard prefactor was calculated for a number of transitions within this research project, it was not applied to any KMC simulations due to time limitations; it is generally accepted that $10^{13}$ is a good estimation of the prefactor for many transitions, and this is demonstrated to be approximately true for 5 critical transitions in Chapter 6. As such the prefactor was assumed to be $10^{13}$ where applicable throughout this research project.

5.1.1 Assembling the KMC

If we know the attempt frequency of a given transition at a desired temperature, we need only provide the full set of potential transitions from a given configuration in order to determine the relative probability of a particular transition occurring along with associated time-scale. Thus we have all the ingredients to perform a KMC simulation:

1. For a given configuration, produce a list of all possible events available. In the Cu ad-atom case given above, it is the 4 possible diffusion directions for the defect.
2. For each transition barrier, calculate the corresponding transition rate using the Arrhenius equation, along with the sum of all rates $R$.
3. Generate a random number, $P$ between 0 and $R$.
4. Cumulatively step through all events until we exceed $P$.
5. The current transition is selected and the system is moved forward one step.
6. The time evolution for the performed step is given by $\delta t = -\frac{\log u}{R}$, where $u$ is a random number between 0 and 1.
7. Return to step 1.

Due to crystal symmetry it is often necessary to find transitions from a few configurations as all other sites are symmetrically equivalent. Thus in the case of simple defect diffusion it is easy to see why KMC is appealing compared to classical MD due to the massively improved simulation times, whilst producing correct probabilistic behaviour. However, as the complexity of the simulation
5.1. KINETIC MONTE CARLO

CHAPTER 5. LONG TIME-SCALE DYNAMICS

increases, so does the difficulty of performing accurate KMC runs. When multiple defects are involved it is necessary to compile very large lists of possible configurations, or approximations are required undermining the accuracy of the simulation. In addition as described previously, predefining the list of possible transitions means that the reaction co-ordinates are forced onto a rigid mesh of potential sites, with little freedom for strain or other effects. As such KMC is a poor candidate for growth modelling where surfaces can become complex with dangling atoms attached by single bonds and atomic arrangements that do not correlate to rigid discretised arrays.

A means of providing some degree of KMC acceleration while allowing for dynamic lattice behaviour that does not conform to discretised relaxation sites, called dynamic or on-the-fly KMC has been developed and applied within this research project.

5.1.2 on-the-fly KMC

In 2001 Henkelman and Jönsson proposed the on-the-fly KMC (OTF-KMC) method as a means to avoid the manual cataloguing of 100s of potential transitions for each lattice configuration [48]. Rather than humanly deriving the table of potential configurations and moves between states, it was possible to use a transition finding algorithm to find a fresh set of potential moves for each new state, thereby allowing for far greater complexity in addition to potentially unforeseeable novel behaviour that would be missed using classical KMC. Figure 5.2 demonstrates the stages of the on-the-fly KMC at the most basic level.

As described previously, when using a transition search algorithm it is necessary to limit the configuration search space. This is achieved through locating defects within the lattice and including only those atoms that are within or in the neighbourhood of the defect. The means employed for locating defects within this research project has involved comparison of an input lattice of interest.

Figure 5.2: The most fundamental steps of an on-the-fly KMC algorithm.

As described previously, when using a transition search algorithm it is necessary to limit the configuration search space. This is achieved through locating defects within the lattice and including only those atoms that are within or in the neighbourhood of the defect. The means employed for locating defects within this research project has involved comparison of an input lattice of interest.
to a perfect lattice. All atoms within the input lattice are compared to those within the reference lattice and any atoms that are not within a ‘vacancy radius’ are considered to be defects of some sort, i.e. interstitial or ad-atoms. Similarly any atoms within the reference lattice that do not correlate to those in the input lattice are considered to be the centre of a vacancy.

Having constructed a vector that contains the indices of those atoms that are actively driven by our search algorithm, the search is initialised. In Henkelman’s original paper he suggests the use of the dimer method, however when dealing with some more complex systems it seems that the RAT method achieves a greater success, particularly when dealing with potentials containing choppy surfaces.

**Transition Searches**

It is not clear how many transition searches are required before we can be confident that the full set of energetically accessible transitions have been located, for example Henkelman stated that when investigating Al diffusion, 50 searches would be the minimum necessary to have confidence that diffusion processes were being explored realistically [49] with an 80% probability of finding the 4 lowest diffusion barriers. It is clear that the number of potential moves for a given system is going to be configuration dependent; 2 ad-atoms have a greater number of moves available than 1, for example. Factors that play a role on the number of searches that would be required for each step include:

- The number of defects.
- The complexity of the potential (metastable configurations, interstitial relaxation, etc.).
- The type of defect.
- The number of atoms in the search vector (i.e. the size of configuration space).

While it might be possible to employ a fixed number of searches as Henkelman and others have previously suggested, this will either result in extreme inefficiency, where the same barriers are found many times, or inaccuracy as crucial barriers are missed before the system evolves to the next step. For the purposes of this research project a new means of determining when the number of searches has been satisfied was developed. Through using a time based termination criteria, the number of unique transitions that were found increases with the complexity of the configuration space. An upper
limit on the search time is set, typically 20 minutes and as the transition searches are spawned the counter is started. Every time a valid saddle-point and corresponding minimum is found, the final configuration is compared to all previously found final states for this particular initial configuration. If the newly found minimum is unique the counter is reset and a new transition search is started. Once the full set of accessible barriers has been found the algorithm begins to find the same barriers over and over again until the time is exceeded and the transition searches are terminated. An upper limit on the number of transitions was also implemented, however this was to allow tuning of the performance of the KMC with the compromise of effecting accuracy.

In order to sustain the performance of the RAT method as the configuration space increases due to the increasing numbers of deposited atoms, it is necessary to scale the size of the translation steps during the search algorithm. By making the maximum translational step-size dependent on the square root of the number of atoms within the search vector, consistent performance was achievable using the RAT technique from 10s to 100s of actively driven search atoms.

Parallelisation

![Parallelisation Diagram](image)

Figure 5.3: The client/server model for the parallelisation of transition searching, minimisation and barrier calculation.

Figure 5.3 demonstrates the operation of the algorithm implemented for this research project which allowed transition searches to be performed in parallel. The parallelisation was performed by a Perl script which handled copying files to each node, executing transition searches, lattice minimisation and barrier finding using the NEB in parallel on as many nodes as were required, although the upper
limit for this research project was 32 processors. It was generally found that a coarse transition search, coupled with the use of the NEB to converge on the saddle point was more efficient than using a refined transition search to find the barrier more accurately. While the NEB is mentioned explicitly, it was also possible to use the DHS and string methods, however in most cases the NEB gave the best performance while also allowing all potential transitions to be visualised through the addition of the MEP.

External Events

The methodology described above will allow for modelling of the evolution of defects in a closed system, however it is often necessary to introduce some external event in order to accurately simulate a problem. In the case of growth modelling it was necessary to allow for depositions to occur within the KMC framework. This was achieved by adding an additional external event to the MC roulette wheel, such that there was some probability of performing an external action at each step of the KMC, with the likelihood of that event being chosen dependent on the relative probabilities of the lattice transitions.
Chapter 6

Binding Sites and Barriers

The implementation of the Hallil et al., and Matsui and Akaogi potentials was discussed in a previous chapter and we now attempt to assess their relative performance through comparison to DFT [51] and experimental results where possible. The DFT modelling was performed using PLATO (Package for Linear Combination of Atomic Orbitals) [56] using the LDA functional, with pseudopotentials and a triple numeric set of atom-centred basis functions with double polarisation, (TNDP). Ed Sanville performed the DFT calculations included in this research project, however, he concluded his position before completion of this thesis. As such some DFT transition barriers are unavailable. Having identified some problems with the original QEq potential some modifications are introduced that allow the formation of surface O$_2$ molecules while penalising excessive charge transfer in the form of a modified QEq potential. Transition barriers are calculated between binding sites where possible using all 3 empirical potentials along with the DFT method and some conclusions are drawn regarding the accessibility of the transitions within the time-frames and temperatures being considered. Finally the prefactors associated with certain key transitions are calculated to assess the suitability of assuming a fixed prefactor for the purpose of calculating transition rates. While DFT+LDA has been shown to provide realistic behaviour for a wide variety of materials [15] it is necessary to note that DFT only provides an approximation to realistic behaviour due to limitations of the model, such as the inability to reproduce electron excitation.
6.1 Modifications to the QEq

Preliminary investigations into the performance of the fixed charge and variable charge potentials revealed some issues when comparing to DFT results. It appeared that the formation of an O\textsubscript{2} molecule on the (110) surface trench might be crucial to surface growth due to relatively low diffusion barriers when using DFT, while simulations of the magnetron plasma suggested O\textsubscript{2} bombardment was more probable than individual atomic oxygen impacts [67]. Additionally, the binding energy of the Ti interstitial was found to be significantly overestimated when using the QEq model compared to DFT results.

6.1.1 Attractive O\textsubscript{2} potential

With no attractive O\textsubscript{2} potential the variable charge potential is unable to reproduce 2 important binding sites, an O\textsubscript{2} ad-molecule resting within the trench, shown in Figure 6.15, and an oxygen atom combining with an ad-row oxygen to form another O\textsubscript{2} molecule, shown in Figure 6.14. Whilst the O\textsubscript{2} in the ad-row can probably be neglected as it is likely not conducive to further growth dynamics, the O\textsubscript{2} molecule in the trench was considered highly important in the rutile growth process - due to the mobility of the O\textsubscript{2} unit.

A modification to the O-O potential was required such that the bulk parameters remained largely unchanged whilst allowing an attractive interaction at the surface of the lattice. This was achieved by creating a many-body potential which switched between an attractive Lennard-Jones potential [53] between the oxygen atoms at the surface and the repulsive Buckingham potential within the bulk.

Figure 6.1 shows 2 oxygen atoms, \textit{i} and \textit{j} with a titanium atom neighbour \textit{k}. For every pair of oxygen atoms i – j a Screening factor for all neighbours, \textit{k}, of \textit{i} and \textit{j} is calculated:

\[
\text{Screening}(r_{ik}) = 0.5 + \frac{\cos(\pi(r_{ik} - r_{ik,\text{cutoff} - \text{min}}) / (r_{ik,\text{cutoff} - \text{max}} - r_{ik,\text{cutoff} - \text{min}}))}{2} \tag{6.1}
\]

\(r_{ik,\text{cutoff} - \text{min}}\) and \(r_{ik,\text{cutoff} - \text{max}}\) describe the screening cut-off ranges and are dependent on the species of \textit{k}, being 0.5 Å to 2.2 Å for Ti and 1.5 Å to 3.0 Å for oxygen respectively.

Once the Screening factor has been calculated for all neighbours \textit{k}, a combined Switching factor is calculated, from which the potential \(V_{ij}\) be evaluated:
6.1. MODIFICATIONS TO THE QEQ

CHAPTER 6. BINDING SITES AND BARRIERS

Figure 6.1: i & j represent 2 oxygen atoms and k a titanium atom.

\[
Switching(r_{ij}, r_{ik}) = \prod_{k=1}^{n} Screening(r_{ik}) \times \prod_{k=1}^{n} Screening(r_{jk})
\]

\[
V_{ij} = Switching \times (LJ(r_{ij}) - Buck(r_{ij})) + Buck(r_{ij})
\]

(6.2)

It is clear that with no neighbours the Switching function will evaluate to zero and therefore the interaction will be purely Lennard-Jones, whilst if a large number of neighbours lie within the cut-off range the screening will be very close to 1 and therefore the interaction purely Buckingham.

The LJ potential was originally parameterised to produce the full O\(_2\) binding energy of 5.2 eV, along with the O\(_2\) bond length of 1.2 Å. Unfortunately this resulted in an inflated O\(_2\) disassociation barrier compared to DFT results and it was necessary to reduce the binding energy to 1.6 eV before similar behaviour was seen. The final parameters of the LJ potential were \(\epsilon = 0.8\) and \(\sigma = 1.05\) Å.

Assuming the titanium atom in Figure 6.1 provides a screening of 0.85, the Buckingham, LJ and combined potentials for \(r_{ij}\) are shown in Figure 6.2, where the red ‘Switched Bond’ curve demonstrates the damped attraction 2 neighbouring oxygen atoms experience.
6.1. MODIFICATIONS TO THE QEQ

6.1.2 Oxygen Hardness

During the testing of the QEq potential a number of problems with charge transfer were observed. The binding energy of the Ti interstitial was found to be much higher than indicated by the DFT results whilst the O$_2$ binding energy in the vicinity of a Ti interstitial was lower than expected. The high binding energy of the Ti interstitial was particularly concerning as it was likely to result in impaired growth modelling as the Ti interstitials would struggle to anneal.

Comparison to DFT data indicated the charge transfer between atoms was higher than desired. By altering the oxygen hardness, i.e. increasing the slope of the quadratic charge acquisition penalty function, it is straightforward to decrease the charge transfer. Bader analysis [86] was used to ascertain the charge on atoms in the neighbourhood of a Ti ad-atom and Ti interstitial, with the results then used to provide the fitness function for the optimisation of the oxygen hardness. Optimising the charges compared to the DFT results led to the oxygen hardness being increased from 12.162 to 18.3 eV; the effects of the hardness change can be readily seen in Figures 6.3 and 6.4. Bader analysis provides only an approximation of the total electronic charge of an atom as there is no quantum mechanical concept of atomic point charge, however the method is consistent and can be reproduce experimentally via electron diffraction analysis. Having modified the oxygen hardness the typical peak charge variation between binding sites was approximately 15% while peak charge variation during
deposition simulations could be up to 60%.

Both figures are shown on the same normalised scale reflecting a range from -1.6 to 2.5 e, where e is the absolute charge on an electron. The relative change in charge transfer on the Ti interstitial is greater than the relative change in charge on the bulk atoms thus decreasing the binding energy of the Ti interstitial. While Hallil et al. parameterised the oxygen hardness using experimental data [41], their modifications to the hardness reduced the value from the original Rappè and Goddard result [81] and thus our modified hardness lies closer to the originally predicted value than the Hallil et al. hardness.

## 6.2 Lattice Properties

Experimentally it is hard to determine binding energies and specific transition barriers due to the length and time scales involved, however the experimentally derived lattice parameters are well known and have been calculated to a good accuracy. The calculation of the lattice parameters along with the bulk modulus is a common preliminary assessment of the performance of an empirical potential.

The minimum energy lattice parameters were found for our empirical potentials by creating a $6 \times 3 \times 3$ tessellation of the primitive TiO$_2$ unit cell and using PBCs and a steepest descent minimisation of the $a$, $c$ and $u$ parameters with numerical estimation of the derivatives.
Table 6.1: The lattice parameter, internal atom position and bulk modulus of rutile TiO$_2$ calculated using the 3 empirical potentials compared to experiment [1].

The maximum error in lattice parameter for both empirical potentials is satisfactory. Hallil et al. found the maximum error to be -0.7% in the \( u \) parameter rather than -1.28% in \( c \) however this difference is difficult to assess without knowing more details of their simulation methods such as the use of boundary conditions, the method for calculating electrostatic forces and the tolerance of the charge minimisation. While the maximum absolute error in the fixed charge potential is greater than that of the QEq model, the mean error in the QEq is larger and the bulk modulus of the fixed charge potential is excellent. The modified QEq potential provides a slightly closer match to the experimental lattice parameters than the original QEq potential.

6.3 Binding Sites

While it is important to reproduce reasonable lattice parameters and compressibilities using an empirical potential, in the case of modelling surface growth it is more important that the correct binding sites are reproduced with the correct ordering of binding energies, otherwise realistic growth behaviour will not be achieved. DFT was used to find the valid binding sites for TiO$_2$, TiO, Ti, O and O$_2$ in order to ascertain the stable sites with which to benchmark our empirical potentials.

6.3.1 TiO$_2$

The TiO$_2$ cluster was found to relax in two configurations on the lattice surface. The most intuitive, TiO$_2$-I relaxation site for the TiO$_2$ cluster, shown in Figure 6.5, places both oxygen atoms above adjacent 5-fold co-ordinated Ti atoms and the Ti ad-atom between two adjacent oxygen atoms in the oxygen ad-row, a site referred to as the ‘upper hollow’. A less stable, TiO$_2$-II configuration, shown in Figure 6.6 leaves a single oxygen atom dangling above the Ti ad-atom.
6.3. BINDING SITES

Whilst most binding sites on the TiO$_2$ surface can be intuitively guessed, it is important to investigate the potential energy surface through alternate means such as classical molecular dynamics and transition barrier searches. The TiO$_2$-II binding site was first seen when performing molecular dynamic deposition of low energy TiO$_2$ molecules on the rutile [1 1 0] surface and had not previously been predicted. Once found to be a minima when using an empirical potential the lattice configuration was simulated in DFT and also found to be stable.

6.3.2 Ti Ad-atom

Once again both types of empirical potentials and the DFT simulation produce two distinct binding sites. The first places the Ti-I ad-atom between 2 successive oxygen atoms in the oxygen ad-row and above an oxygen in the trench surface, within the ‘upper hollow’, shown in Figure 6.7. The second Ti-II site, shown in Figure 6.8, is physically lower and places the Ti ad-atom between 2 oxygen atoms in the trench, adjacent to an ad-row oxygen, a site referred to as the ‘lower hollow’.

While the fixed charge potential finds both Ti minima the Ti-II configuration results in a large degree of surface distortion.
6.3. BINDING SITES

6.3.3 Ti Interstitial

The DFT, QEq and MQEq methods produce 2 distinct binding sites for the Ti interstitial, with the fixed charge potential reproducing neither. The first Ti-i-I site places the Ti atom directly below a surface oxygen in what is equivalent to the upper hollow binding site while the second Ti-i-II interstitial location leaves the Ti interstitial directly between 2 surface oxygen atoms adjacent to the ad-row oxygen, this is equivalent to the lower hollow binding site. Whilst there is differentiation of the interstitials close to the lattice surface, the 2 sites are spatially equivalent representing a rotation of the crystal about the [0 0 1] axis of 90°.

Unfortunately attempts to relax the interstitials using the fixed charge potential resulted in surface reconstruction with an exchange process resulting in a Ti ad-atom.

6.3.4 TiO

There are four unique binding sites for the TiO cluster on the rutile surface. The TiO-I and TiO-III ad-units both have the Ti atom relaxing in the upper hollow with the TiO-I unit relaxing the oxygen above the adjacent 5-fold co-ordinated Ti atom, as shown in Figure 6.9, and the TiO-III leaving the oxygen atom dangling above the Ti ad-atom much like the TiO$_2$-II unit, shown in Figure 6.10.
Similarly the TiO-II, shown in Figure 6.11, and TiO-IV units have a common Ti ad-atom relaxing in the lower hollow with the TiO-II atom having an oxygen above an adjacent 5-fold co-ordinated Ti and the TiO-IV leaving the oxygen dangling, as seen in Figure 6.12.

The QEq potential reproduces all four binding sites successfully while the fixed charge and MQEq
potentials fail to relax in the TiO-III and TiO-IV configurations. As in the case of the Ti-II binding site, the placement of a Ti ad-atom in the lower hollow using the fixed charge potential results in a large degree of lattice distortion around the defect.

### 6.3.5 Oxygen

The most obvious binding site for an oxygen atom is directly above the 5-fold co-ordinated Ti in the O-I configuration as shown in Figure 6.13. An additional, less intuitive O-II, site binds the oxygen ad-atom to an oxygen from the ad-row to form an O$_2$ molecule, shown in Figure 6.14.

![Figure 6.13: O-I defect from the [1 1 0] and [1 0 0] directions.](image)

![Figure 6.14: O-II defect from the [1 1 0] and [1 0 0] directions.](image)

While the DFT results indicate that the O-II configuration is energetically favourable, it is not possible to reproduce the binding site using the fixed charge and QEq potentials due to the lack of an attractive O-O component. The MQEq potential succeeds in reproducing both binding sites, however, it produces an incorrect energetic ordering as shown in Table 6.2.

### 6.3.6 O$_2$

A single binding site is found for a depositing O$_2$ ad-unit. Figure 6.15 shows a single oxygen bound to a 5-fold co-ordinated Ti atom with the other oxygen dangling above the surface.
As with the O-II binding site, the O$_2$-I ad-molecule cannot be reproduced using the fixed charge and QEq potentials, however, it is stable using the MQEq potential.

### 6.4 Binding Energy

Once settled on a final form of the MQEq potential the binding energies for the minimum energy configurations seen in Section 6.3 were calculated and compared. Table 6.2 shows the relative and absolute binding energies for the previously described ad-units on the rutile surface.

<table>
<thead>
<tr>
<th>Binding Site</th>
<th>Fixed Charge</th>
<th>QEq</th>
<th>MQEq</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-I</td>
<td>0 (-6.92)</td>
<td>0 (-5.99)</td>
<td>0 (-5.85)</td>
<td>0</td>
</tr>
<tr>
<td>TiO$_2$-II</td>
<td>1.54 (-5.38)</td>
<td>0.292 (-5.70)</td>
<td>1.08 (-4.77)</td>
<td>1.11</td>
</tr>
<tr>
<td>Ti-I</td>
<td>0 (-12.4)</td>
<td>2.34 (-11.8)</td>
<td>1.51 (-8.91)</td>
<td>1.91</td>
</tr>
<tr>
<td>Ti-II</td>
<td>0.671 (-11.8)</td>
<td>2.89 (-11.2)</td>
<td>2.06 (-8.37)</td>
<td>2.82</td>
</tr>
<tr>
<td>Ti-i-I</td>
<td>N/A</td>
<td>0.069 (-14.0)</td>
<td>0.168 (-10.3)</td>
<td>0</td>
</tr>
<tr>
<td>Ti-i-II</td>
<td>N/A</td>
<td>0 (-14.1)</td>
<td>0 (-10.4)</td>
<td>0.26</td>
</tr>
<tr>
<td>TiO-I</td>
<td>0 (-8.89)</td>
<td>0.0085 (-8.11)</td>
<td>0 (-6.72)</td>
<td>0</td>
</tr>
<tr>
<td>TiO-II</td>
<td>1.05 (-7.84)</td>
<td>0.490 (-7.63)</td>
<td>0.395 (-6.32)</td>
<td>0.85</td>
</tr>
<tr>
<td>TiO-III</td>
<td>N/A</td>
<td>0 (-8.12)</td>
<td>N/A</td>
<td>0.61</td>
</tr>
<tr>
<td>TiO-IV</td>
<td>N/A</td>
<td>0.612 (-7.51)</td>
<td>N/A</td>
<td>1.32</td>
</tr>
<tr>
<td>O-I</td>
<td>0 (-4.86)</td>
<td>0 (-2.00)</td>
<td>0 (-4.37)</td>
<td>0</td>
</tr>
<tr>
<td>O-II</td>
<td>N/A</td>
<td>N/A</td>
<td>3.76 (-0.613)</td>
<td>1.08</td>
</tr>
<tr>
<td>O$_2$-I</td>
<td>N/A</td>
<td>N/A</td>
<td>0 (-5.91)</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 6.2: Binding Energies (eV): Relative (Absolute)

The absolute binding energy is calculated by taking the energy of the lattice with the cluster bound to the surface and subtracting the energy of the cluster in a vacuum and the energy of the perfect substrate. Some of these binding energies have been previously published by Ed Sanville et al. [87].

6.4.1 Conclusions

The performance of the Matsui and Akaogi fixed charge potential is surprisingly good considering it was only parameterised to reproduce the cell parameters, molar volume and mean Ti-O distance at 300K. While not designed for modelling surface behaviour, the relative binding energies of the ad-clusters are reasonable when compared to DFT results although the effect of using full charges on ad-atoms is particularly evident due to the surface distortion in the region of a Ti-II ad-atom, or the reconstruction when relaxing a Ti interstitial. The original Hallil et al., potential is impressive in that it is able to reproduce all the binding sites found using DFT that do not involve an O$_2$ molecule, however, it fails to predict the energetic ordering of the TiO binding sites correctly. The MQEq potential introduces some artefacts; the TiO-III and TiO-IV binding sites are no longer stable and collapse into TiO-I and TiO-II configurations respectively, the binding energy of the Ti-II ad-atom is less accurate than when using the original QEq method compared to DFT results and the O-II binding energy is very different to the DFT predicted result. However the TiO$_2$ binding energy is more accurate, the TiO binding energies are now ordered correctly and the important O$_2$ molecule binding to the surface is reproduced.

6.5 Transition Barriers

A large number of transitions involving simple clusters or ad-atoms on the rutile (1 1 0) surface have been investigated. The NEB or string method was used to find the barrier peak along with the MEP to allow comparison between the DFT, FC, QEq and MQEq where possible. When relaxing the NEB and string methods 10 nodes were used along with a climbing image to provide the precise barrier peak while 100 line minimisations were used for the NEB and 200 minimisations steps for the string method in order to ensure convergence. Through calculating the barriers associated with several
important transitions it should be possible to provide an insight into likely diffusion mechanisms that will contribute to further rutile (1 1 0) crystal growth.

Where relevant the transition rate has been calculated using Eyring’s transition state theory [32] using an assumed fixed prefactor of $10^{13}$ and a qualitative comparison of the transitions accessibility is given at 300 K which is typical of the temperatures within the sputtering process. In order to qualify a transition as accessible within the industrial time-scales it is necessary to know the deposition rate of TiO$_2$ units during the magnetron sputtering process. A typical TiO$_2$ growth rate corresponds to a deposition rate of roughly 0.25 TiO$_2$ units Å$^{-2}$ s$^{-1}$, or 0.75 atoms Å$^{-2}$ s$^{-1}$ [36, 71], while the density of the TiO$_2$ rutile (1 1 0) surface is approximately one atom per 4 Å$^2$. A crude gauge of whether a transition is accessible within relevant time-scales and temperatures is to require that the probabilistic frequency of a transition is higher than the deposition incidence rate per surface atom; therefore the frequency of the transition should perhaps be greater than 3 Hz. At 300 K this equates to a transition barrier of 0.75 eV, however in practice local temperature spiking due to incident sputtered atoms will allow for some higher energy transitions to occur; for the purposes of this section a barrier of 1 eV or lower is considered to be accessible.

While the bulk of the transitions are intuitive and were straightforward to derive, some were first observed using the transition search methods described previously while others were observed during deposition simulations.

### 6.5.1 TiO$_2$

TiO$_2$ cluster diffusion along the surface warrants initial investigation as the binding sites are well represented by all empirical potentials along with DFT. The TiO$_2$-I cluster can move into an equivalent TiO$_2$-I configuration via 3 mechanisms.

**TiO$_2$-I to TiO$_2$-Ia**

The first and most obvious transition is the simple slide of the TiO$_2$ unit up the the surface trench in the [0 0 1] direction as shown in Figure 6.16, where transition atoms are highlighted in yellow.

Figure 6.17 shows the NEB calculations for the TiO$_2$-I to TiO$_2$-Ia transition using all 3 empirical potentials compared to the DFT results. The overall shape and total Euclidean distance between the initial and final configurations varies only slightly as the lattice parameters differ only marginally.
Figure 6.16: TiO$_2$-I to TiO$_2$-Ia: The ad-molecule travels up the surface trench in the $[001]$ direction.

from the experimental values. In this stoichiometric configuration the fixed charge potential provides the closest match to the DFT results, whilst the QEq potential provides the poorest. The increase in energy required to undergo the transition when using the MQEq method is largely due to the increased oxygen hardness, the oxygen ad-atom acquires 0.68 e charge in the QEq method, rising to 0.73 e using the modified potential thereby increasing the repulsive force between the ad-oxygen and surface oxygen atoms.

A 38.33% deviation in barrier between DFT and the MQEq model might provide some cause for concern when using the variable charge potential, however in reality the 2.36 eV barrier is equally as inaccessible as a 3.26 eV barrier at the temperatures and time-scales being considered within this research.

Figure 6.17: TiO$_2$-I to TiO$_2$-Ia transition using the FC, QEq, MQEq and DFT models.
6.5. TRANSITION BARRIERS

**TiO$_2$-I to TiO$_2$-Ib**

The second transition between TiO$_2$-I configurations involves the inversion of the Ti ad-atom across the trench in the [1$ar{1}$0] direction, while the oxygen atoms remain fixed as shown in Figure 6.18

![Initial configuration](image1)
![MEP peak](image2)
![Final configuration](image3)

Figure 6.18: TiO$_2$-I to TiO$_2$-Ib: The Ti ad-atom crosses trench in [1$ar{1}$0] direction.

<table>
<thead>
<tr>
<th>Separation (Å)</th>
<th>FC</th>
<th>QEq</th>
<th>MQEq</th>
<th>DFT</th>
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<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
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</tr>
<tr>
<td>1.0</td>
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<td>2.5</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Figure 6.19: TiO$_2$-I to TiO$_2$-Ib transition using FC, QEq, MQEq, and DFT.

Unfortunately the MQEq potential performs the worst in terms of the peak barrier when compared to the other empirical potential models, as demonstrated in Figure 6.19, however, it is does capture the asymmetry of the DFT with the MEP peak correlating very closely. An artefact of the original QEq potential is that the the midpoint of the transition is a valid minima with an escape barrier of several tenths of an eV, although in practice the Ti atom will escape extremely rapidly in comparison to the frequency of the entire transition. As with the TiO$_2$-I to TiO$_2$-Ia transition the fixed charge potential provides behaviour that is closest to the DFT results, while all the barriers are outside the time-scales involved in the typical growth process.
6.5.2 TiO$_2$-I to TiO$_2$-Ic

The third transition between symmetrically equivalent TiO$_2$-I configurations involves the entire TiO$_2$ molecule flipping over the oxygen ad-row in the $\overline{1}10$ direction as shown in Figure 6.20.

![Initial configuration](image1)
![MEP peak](image2)
![Final configuration](image3)

Figure 6.20: TiO$_2$-I to TiO$_2$-Ic: The TiO$_2$ molecule rotates about oxygen ad-row in $\overline{1}10$ direction.

![Barrier vs Separation](image4)

Figure 6.21: TiO$_2$-I to TiO$_2$-Ic transition using FC, QEq, MQEq, and DFT.

Figure 6.21 reveals that once again the fixed charge model provides the closest approximation to the DFT barrier while the MQEq model provides the closest match in terms of characteristic shape. The traditional QEq potential performs very poorly and underestimates the correct barrier but in practice all methods produce peak barriers that are inaccessible at the typical industrial energies and temperatures we are interested in.

**TiO$_2$-I to TiO$_2$-II**

There is a single symmetrically unique mechanism by which we can migrate from a TiO$_2$-I to TiO$_2$-II configuration shown in Figure 6.22 where a single oxygen molecule detaches from its corresponding
6.5. TRANSITION BARRIERS

Ti trench atom to rest directly above the Ti ad-atom.

Figure 6.22: Oxygen atom detaches from the trench and comes to rest above the Ti ad-atom.

Figure 6.23: TiO$_2$-I to TiO$_2$-II Transition using FC, QEq, MQEq, and DFT

Not only does Figure 6.23 demonstrate a considerable difference between the relative energies of the 4 models, but the total Euclidean separation between the initial and final configurations also varies considerably. The difference when using the DFT and FC methods versus the QEq and MQEq methods are due to differing floating oxygen relaxation points in the TiO$_2$-II configuration. For the first time the fixed charge model does not provide the closest correlation to the DFT results due to a large overestimation of the transition barrier, with the TiO$_2$-II configuration highly energetically unfavourable. The MQEq method provides an excellent correlation with both the characteristic shape of the DFT MEP and the overall energy barrier, while the QEq potential provides a very poor estimation of the barrier, making the transition highly accessible at the temperatures and energies being considered.
6.5. TRANSITION BARRIERS

TiO$_2$-II to TiO$_2$-IIa

There are three mechanisms by which a TiO$_2$-II ad-cluster can migrate along the rutile surface, while remaining in a symmetrically equivalent configuration. The first allows the molecule to travel between adjacent trenches and involves the TiO$_2$ molecule flipping over the oxygen ad-row as shown in Figure 6.24.

![Initial configuration, MEP peak, Final configuration](image)

Figure 6.24: TiO$_2$-II to TiO$_2$-IIa: The TiO$_2$-II unit rolls over the oxygen ad-row.

![Barrier vs Separation](image)

Figure 6.25: TiO$_2$-II to TiO$_2$-IIa transition using FC, QE, MQE, and DFT.

Unlike in the case of the previous transitions, Figure 6.25 demonstrates that all three empirical potentials provide a poor approximation of the DFT results for the TiO$_2$-II to TiO$_2$-IIa transition. The relative behaviour of the empirical potentials is surprisingly correlated compared to previous transition barriers and renders them all accessible within typical industrial energies and time-scales, in stark contrast to the result predicted using DFT.
6.5. TRANSITION BARRIERS

Chapter 6. BINDING SITES AND BARRIERS

TiO$_2$-II to TiO$_2$-IIb and TiO$_2$-II to TiO$_2$-IIc

Once in the TiO$_2$-II configuration the ad-molecule can travel along the trench by undergoing two steps, first the molecule can rotate about the Ti ad-atom as shown in Figure 6.26 and secondly the Ti and floating oxygen can hop over the adjacent surface oxygen as shown in Figure 6.28.

(a) Initial configuration  
(b) MEP peak  
(c) Final configuration

Figure 6.26: TiO$_2$-II-TiO$_2$-IIb: TiO$_2$-II rotates about the ad-Ti atom.

While the MQE$\text{q}$ provides the closest fit to the DFT result, shown in Figure 6.27, it still massively underestimates the barrier rendering the transition accessible within the time-scales considered. The FC model is particularly poor indicating the transition could occur with a very high frequency.

Unfortunately the DFT results are unavailable for the TiO$_2$-II to TiO$_2$-IIc transition. However, the barriers, shown in Figure 6.29, produced using the empirical potentials are much like those seen in the other TiO$_2$-II cases; the fixed charge potential is extremely low once again making the migration of a TiO$_2$-II molecule along the trench highly accessible within the time-scales considered. The QE$\text{q}$
6.5. TRANSITION BARRIERS

(a) Initial configuration  (b) MEP peak  (c) Final configuration

Figure 6.28: TiO$_2$-II to TiO$_2$-Ic: The ad-Ti atom hops over adjacent trench oxygen.

Figure 6.29: TiO$_2$-II to TiO$_2$-Ic transition using FC, QEq, and MQEq.

potential finds a metastable configuration corresponding to the Ti ad-atom relaxing within the lower hollow while the MQEq does not. This is surprising as both potentials produce a similar TiO-II binding configuration.

6.5.3 TiO

The TiO ad-molecule is unlike the TiO$_2$ cluster in that not all binding sites are reproducible using the empirical and DFT models. While the original QEq potential successfully produces all DFT relaxation configurations the FC and MQEq potentials produce TiO-III and TiO-IV configurations that are unstable and will relax into the TiO-I and TiO-II configurations respectively.

TiO-I to TiO-I

The TiO-I binding configuration is the lowest energy site when using DFT modelling. There is a single transition available to the TiO-I ad-cluster that produces a symmetrically equivalent final
configuration; where the oxygen atom detaches from the 5-fold co-ordinated Ti trench atom, hops over the neighbouring trench oxygen and comes to rest over the adjacent Ti atom as shown in Figure 6.30.

![Figure 6.30: TiO-I to TiO-Ia: Ad-oxygen hops over trench oxygen to adjacent 5-fold Ti site.](image)

The modifications to the QEq potential result in a correlation between the fixed charge and the MQEq model, shown in Figure 6.31. Despite the nonstoichiometric configuration the fixed charge potential produces a sensible barrier. The QEq model severely underestimates the DFT barrier rendering an event which has a low probability, highly frequent at the temperatures considered. The larger Euclidean displacement when using DFT is due to a longer bond-length between the Ti and O ad-atoms.

**TiO-I to TiO-II**

The TiO-I to TiO-II transition involves the oxygen ad-atom remaining fixed above the 5-fold co-ordinated Ti atom whilst the Ti ad-atom hops over the surface oxygen into the adjacent minimum,
shown in Figure 6.32.

Figure 6.32: TiO-I to TiO-II: The Ti atom hops over the trench oxygen into the adjacent minima.

Figure 6.33: TiO-I to TiO-II transition using FC, QEq, and MQEq

As with the oxygen disassociation in the TiO\textsubscript{2}-I to TiO\textsubscript{2}-II transition, the fixed charge model predicts a large barrier compared to the other models, as shown in Figure 6.33, while both variable charge potentials produce similar results. The difference in Euclidean displacement between the models is due to a large degree of surface reconstruction when the Ti ad-atom is in the lower hollow using the fixed charge potential.

**TiO-I to TiO-III**

The TiO-III is the first of 2 TiO binding configurations which are only available when using the original QEq model as the MQEq potential relaxes the TiO-III and TiO-IV into the TiO-I and TiO-II configurations respectively. The TiO-I to TiO-III transition is demonstrated in Figure 6.34.

Unfortunately despite finding a valid binding site the QEq potential, shown in Figure 6.35, provides
an incorrect ordering of binding energy as shown previously. At the temperatures being considered the relative difference in predicted frequency, using the Arrhenius equation to predict the attempt frequency at industrial temperatures, is $1.35 \times 10^8$ which is significant enough to suggest the simulated growth dynamics would be incorrect if this was a critical growth transition. The DFT behaviour is unusual in that the potential surface plateaus with a region of choppy metastable configurations before finding the valid minimum.

**TiO-II to TiO-IV**

The lowest energy TiO-II transition demonstrates the formation of the TiO-IV configuration through the detachment of the ad-oxygen from the 5-fold co-ordinated Ti as shown in Figure 6.36.

No DFT results are available for the transition so a comparison to the QEq cannot be provided. As demonstrated by the low barrier shown in Figure 6.37, this transition can occur at high frequency
6.5. TRANSITION BARRIERS

Figure 6.36: TiO-II to TiO-IV: The oxygen atom detaches from the 5-fold co-ordinated Ti trench atom.

Figure 6.37: TiO-II to TiO-IV transition using the QEq potential.

at the temperatures being considered, however, the TiO-IV configuration is extremely unstable.

**TiO-III to TiO-IV**

Once again only reproducible with the QEq model, the TiO-III-TiO-IV transition involves the Ti ad-atom hopping from the upper to lower hollow as shown in Figure 6.38.

Figure 6.38: TiO-III to TiO-IV: The Ti atom hops from the upper to the lower hollow.
Figure 6.39 demonstrates that both the QEq and DFT models produce the same characteristic shape and similar barriers, however it is not surprising to see the QEq method underestimates the DFT barrier once again.

6.5.4 Ti

As described in the previous section there are 2 distinct binding sites for a Ti ad-atom on the rutile (1 1 0) surface along with 2 equivalent interstitial locations.

Ti-I to Ti-I

It is possible for the Ti ad-atom to pass directly between adjacent ad-row oxygen atoms into a symmetrically equivalent configuration as shown in Figure 6.40.

Figure 6.40: Ti-I to Ti-I: The Ti atom hops between the oxygen ad-row atoms.

The DFT and QEq barriers in Figure 6.41 are extremely similar, while the MQEq and fixed
charge models also produce similar barriers. Unfortunately the MQEq predicts the transition as possible but rare at temperatures of interest, while the DFT barrier indicates the transition will be inaccessible. Given the degree of surface distortion seen with the fixed charge potential it is surprising the transition barriers are reasonably accurate.

**Ti-I to Ti-i-I**

This transition involves the Ti ad-atom moving to form an interstitial via an exchange mechanism with a 6-fold co-ordinated Ti ad-row atom as shown in Figure 6.42. This transition is unavailable to the fixed charge model as there is no stable interstitial relaxation point.

One of the goals when increasing the hardness of the oxygen atoms was to decrease the binding energy of the Ti interstitials which is evident in Figure 6.43. While the binding energy has been reduced, the barrier increases bringing the MQEq behaviour closer to that of DFT. In practice the
transition is barely accessible at interesting temperatures when using the variable charge potentials, whilst effectively inaccessible according to DFT.

**Ti-I to Ti-II**

An alternate transition involves the Ti ad-atom making the short hop to the lower hollow as shown in Figure 6.44

![Figure 6.44: Ti-I to Ti-II: The Ti atom hops from the upper to the lower hollow.](image)

Figure 6.44: Ti-I to Ti-II: The Ti atom hops from the upper to the lower hollow.

Figure 6.45 shows the NEB barriers using all 4 modelling methods with the fixed charge model displaying a large Euclidean displacement due the the severe distortion of the lattice surface. The shape of the MQEq and DFT models are well correlated while the barriers for both variable charge potentials are almost identical. Much like those transitions involving an oxygen ad-atom tethered by a single bond, the fixed charge potential performs poorly compared to the DFT result. The high barrier is an artefact of the difference in binding energies between the states with the reverse barrier
readily accessible at industrial deposition temperatures.

**Ti-II to Ti-i-II**

The most readily accessible mechanism for interstitial formation is the direct drop of a Ti-II ad-unit into the Ti-i-II interstitial location as shown in Figure 6.46.

![Figure 6.46: Ti-II to Ti-i-II](image)

The DFT barrier was not available for this transition and hence is not shown in Figure 6.47. While both variable charge barriers correlate well, the MQEq potential once again produces the desired decrease in interstitial binding energy. Despite this it is obvious that the spontaneous formation of a Ti-II ad-unit from a Ti-i-II interstitial is unlikely except at high temperatures by simply viewing the relative binding energies.
6.5. Transition Barriers  

Another intuitively derived transition was the diffusion of the Ti-i-I interstitial between trenches via an exchange mechanism with the 6-fold co-ordinated ad-row Ti atom as shown in Figure 6.48

![Figure 6.48: Ti-I to Ti-Ia](image)

This transition was found to produce extremely high barriers. The MQEq provides the closest match to the DFT result, however, the characteristic of both variable charge potentials are dissimilar to that of the DFT MEP, as shown in Figure 6.49.

**Ti-I to Ti-II**

The most obvious diffusion transition for the Ti-i-I interstitial is the short slide into the adjacent Ti-i-II interstitial location as shown in Figure 6.50.

![Figure 6.50: Ti-I to Ti-II](image)
Figure 6.49: Ti-i-I to Ti-i-I transition using QEq, MQEq, and DFT.

Figure 6.50: Ti-i-I to Ti-i-II: The Ti interstitial slides directly into a Ti-i-II site.

Figure 6.51: Ti-i-I to Ti-i-II transition using QEq, MQEq, and DFT.

should expect to find the binding energy to become equal. It is therefore purely due to surface effects that the binding energy between the sites varies when using the DFT model. Unfortunately neither of

96
the variable charge models capture the energy asymmetry, finding the binding sites nearly equivalent, as shown in Figure 6.51. While the transition is largely inaccessible according to DFT results, both variable charge potentials produce barriers that are likely at temperatures being considered, with the MQEq performing particularly poorly.

6.5.5 Oxygen

Only one binding site is common to all four empirical potentials, where the oxygen relaxes above a 5-fold co-ordinated Ti trench atom as shown in Figure 6.52.

O-I to O-I

From the primary binding site the oxygen can diffuse along the trench by hopping to adjacent 5-fold Ti atoms.

Figure 6.52: O-I to O-I: The oxygen ad-atom hops over the trench oxygen atoms to come to rest over the adjacent 5-fold Ti.

Figure 6.53: O-I to O-I transition using FC, QEq, MQEq, and DFT.
The peculiar barrier produced using DFT, shown in Figure 6.53, is due to the asymmetric relaxation of the oxygen over the 5-fold Ti atom. Surprisingly the small barrier associated with the first half of the transition using DFT is due to the hop between the trench oxygen atoms, while the larger but still small 0.29 eV barrier involves the oxygen ad-atom hopping over the 5-fold Ti atom. According to DFT results ad-oxygen diffusion along the trench should occur with a high frequency at interesting temperatures, however, both variable charge potentials find a barrier that is accessible but less frequent. The fixed charge potential models the transition very poorly, finding an energetically favourable configuration with the ad-oxygen bridging the 2 surface oxygen atoms, while the traditional O-I relaxation point over the 5-fold Ti is metastable.

6.5.6 O-I to O-II

The second binding site for the ad-oxygen involves it combining to form an O$_2$ molecule in the oxygen ad-row as shown in Figure 6.54. This is only captured by the MQEq potential due to the introduction of an attractive component between oxygen atoms.

![Figure 6.54: O-I to O-II: The oxygen ad-atom leaves the trench and forms an O$_2$ molecule with ad-row oxygen.](image)

Despite the success capturing the O-II binding site, the MEP produced by the MQEq, shown in Figure 6.55, does not have any correlation with the DFT results. In addition to incorrectly ordering the relative binding energies of the sites the modified variable charge potential predicts an enormous formation barrier. It is clear from DFT data that an O$_2$ molecule in the ad-row will never disassociate to form an ad-row oxygen plus an oxygen above the 5-fold co-ordinated Ti atom while conversely an oxygen ad-atom will never form an O$_2$ molecule in the ad-row when using the MQEq potential. The messy DFT energy landscape is due to a number of metastable relaxation points along the surface between the O-I and O-II configuration.
6.5.7 O₂

There is only a single transition available for the O₂ molecule which translates the ad-cluster along the trench shown in Figure 6.56.

**O₂-I to O₂-I**

Using the MQEq potential the lowest energy diffusion mechanism involves the O₂ molecule sliding directly up the trench as shown in Figure 6.56, while DFT finds that the O₂ rolling along the trench oxygen atoms provides a lower barrier.

![Figure 6.56: O₂-I to O₂-I transition using MQEq, and DFT.](image)

(a) Initial configuration  (b) MEP peak  (c) Final configuration

Figure 6.56: O₂-I to O₂-I: The oxygen slides along the trench using MQEq and rolls along using DFT.

Most of the transitions described previously will occur with a relatively low frequency within the time-scales being considered due to the size of the barriers and hence it is difficult to conceive how crystal growth can occur with little surface diffusion. The DFT barrier for O₂, shown in Figure 6.57, provides an exception in that the O₂ molecule will be able to diffuse along trenches rapidly within
the deposition timeframe.

Figure 6.57: O\textsubscript{2}-I to O\textsubscript{2}-I transition using MQEq, and DFT.

The O\textsubscript{2} diffusion along the trench is an example of a transition where the NEB fails. During the initial stages of the minimisation process the interpolation places the oxygen atoms outside the basin of mutual attraction and they are repelled from each other. As the NEB proceeds, the spring forces do not compensate for repulsive force and the final MEP indicates the atoms disassociate before recombining, thus in this case it was necessary to use the string method to converge on a meaningful MEP.

The rolling diffusion mechanism found using DFT comprises of 2 distinct steps with very similar energy barriers, while the MQEq effectively consists of a single transition with a small metastable central state where the O\textsubscript{2} molecule bridges the 2 adjacent 5-fold co-ordinated Ti atoms. Unfortunately the energy difference between the barriers indicates that using the DFT model the O\textsubscript{2} molecule would diffuse extremely rapidly at temperatures of interest, with a Arrhenius equation predicted attempt frequency of 7.22 \times 10^{10} Hz, while using the MQEq model the transition is still readily accessible at temperatures of interest but considerably less frequent with a frequency of just 293 Hz.

6.5.8 Mixed Transitions

Some complex transitions that may be important to the TiO\textsubscript{2} growth process are described in this section.
Formation of a TiO$_2$-I unit from 2 lone O-I ad-atoms and a Ti-i-I interstitial

Figures 6.43 and 6.47 demonstrated that once a Ti interstitial has formed, there is little possibility of it escaping due to large escape barriers. Despite this result it is possible to grow rutile TiO$_2$ with a (1 1 0) preferential surface thus there clearly must be an energetically favourable mechanism by which interstitials can escape to form further layer growth. The influence of oxygen ad-atoms in the presence of the Ti interstitial was investigated as shown in Figure 6.58.

Figure 6.58: 2O-II+Ti-i-I to TiO$_2$-I: The Ti-i-I interstitial exchanges with a 6-fold Ti atom to form a TiO$_2$-I unit.

Figure 6.59 demonstrates the change in escape barrier for a Ti interstitial in the neighbourhood of a pair of oxygen ad-atoms. Both the MQEq and the DFT models produce accessible barriers of 0.76 eV and 0.55 eV respectively, while the QEq potential predicts an inaccessible 1.6 eV escape barrier. All three models produce MEPs with similar characteristic shapes with metastable minima corresponding to a configuration where the TiO$_2$ ad-molecule has been formed however the Ti interstitial has not
yet occupied the 6-fold Ti vacancy. The low barriers produced using DFT and the MQEq potential demonstrate that it is possible and even likely that Ti interstitials will anneal within the temperatures and time-scales of interest, conducive to further rutile growth. As it is extremely crucial that a mechanism exists by which the Ti interstitials are able to escape to the surface in order to facilitate surface growth it is significant that this is an improbable transition when using the original QEq model. It is particularly interesting that whilst the MQEq barrier is higher than predicted using DFT, it is very close to the experimentally deduced value of 0.82 eV [60].

**O$_2$-I Dissociation in the Presence of a Ti-I interstitial**

While it has been shown that Ti interstitials are able to escape onto the lattice surface in the neighbourhood of ad-oxygen atoms, this assumes that the O$_2$ disassociation is accessible in the neighbourhood of a Ti interstitial as shown in Figure 6.60.

![Initial configuration](image1)
![MEP peak](image2)
![Final configuration](image3)

Figure 6.60: O$_2$-I+Ti-i-I to 2O-I+Ti-i-I: The O$_2$ molecule separates into 2 O-I ad-atoms in the presence of a Ti interstitial.

![Graph](image4)

Figure 6.61: O$_2$-I+Ti-i-I to 2O-I+Ti-i-I transition using MQEq potential and DFT.
Figure 6.61 demonstrates the $O_2$ disassociation is readily accessible at the temperatures and time-scales being considered, indicating that it is likely the rapidly diffusing $O_2$ ad-molecules and oxygen ad-atoms provide the means by which the readily formed Ti interstitials are annealed.

**Formation of a Ti-i-II split interstitial from a Ti-II ad-atom**

While not conducive to rutile growth, an interesting low energy interstitial formation barrier was found when performing transition searches on a lattice containing a Ti-II ad-atom. It was found that in many cases rather than forming a single Ti-i-II interstitial, the Ti ad-atom would displace the 5-fold co-ordinated Ti atom forming a pair of Ti-i-II split interstitials and a Ti vacancy, as demonstrated in Figure 6.62.

![Figure 6.62: Ti-II to 2Ti-i-II: The Ti-II ad-atom forms a split interstitial competing for the 5-fold Ti vacancy.](image)

Considering the transition introduces an unnecessary defect into the lattice, the transition barrier shown in Figure 6.63 is surprisingly low. The total binding energy is very similar to the formation
6.6 Transition Prefactors

The previous section relied on the commonly made assumption [100] that a typical prefactor for a transition is $10^{13}$. In order to validate this is a reasonable assumption, the prefactor has been calculated for a number of transitions that have been deemed to be important. In order to calculate

<table>
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<th>QEq</th>
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<td>2.71</td>
<td>1.92</td>
<td>2.36</td>
<td>3.26</td>
</tr>
<tr>
<td>TiO$_2$-I to TiO$_2$-Ib</td>
<td>2.48</td>
<td>2.20</td>
<td>2.99</td>
<td>2.96</td>
</tr>
<tr>
<td>TiO$_2$-I to TiO$_2$-Ic</td>
<td>5.44</td>
<td>1.96</td>
<td>1.67</td>
<td>5.03</td>
</tr>
<tr>
<td>TiO$_2$-I to TiO$_2$-Iia</td>
<td>1.96 (0.416)</td>
<td>0.359 (0.073)</td>
<td>1.11 (0.034)</td>
<td>1.27 (0.158)</td>
</tr>
<tr>
<td>TiO$_2$-II to TiO$_2$-Iia</td>
<td>1.02</td>
<td>0.929</td>
<td>0.932</td>
<td>3.51</td>
</tr>
<tr>
<td>TiO$_2$-II to TiO$_2$-Iib</td>
<td>0.224</td>
<td>0.565</td>
<td>0.646</td>
<td>1.37</td>
</tr>
<tr>
<td>TiO$_2$-II to TiO$_2$-Iic</td>
<td>0.338</td>
<td>0.838</td>
<td>0.908</td>
<td>N/A</td>
</tr>
<tr>
<td>TiO-I to TiO-Ia</td>
<td>0.562</td>
<td>0.224</td>
<td>0.525</td>
<td>0.931</td>
</tr>
<tr>
<td>TiO-I to TiO-II</td>
<td>1.23 (0.171)</td>
<td>0.818 (0.369)</td>
<td>0.641 (0.258)</td>
<td>N/A</td>
</tr>
<tr>
<td>TiO-I to TiO-III</td>
<td>N/A</td>
<td>0.226 (0.253)</td>
<td>N/A</td>
<td>0.71 (0.1)</td>
</tr>
<tr>
<td>TiO-II to TiO-IV</td>
<td>N/A</td>
<td>0.174 (0.0031)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TiO-III to TiO-IV</td>
<td>N/A</td>
<td>1.12 (0.468)</td>
<td>N/A</td>
<td>1.48 (0.785)</td>
</tr>
<tr>
<td>Ti-I to Ti-Ia</td>
<td>0.765</td>
<td>1.21</td>
<td>0.708</td>
<td>1.20</td>
</tr>
<tr>
<td>Ti-I to Ti-i-I</td>
<td>N/A</td>
<td>1.01 (3.29)</td>
<td>1.15 (2.61)</td>
<td>1.60 (3.51)</td>
</tr>
<tr>
<td>Ti-I to Ti-II</td>
<td>0.797 (0.126)</td>
<td>1.04 (0.460)</td>
<td>1.08 (0.489)</td>
<td>1.52 (0.611)</td>
</tr>
<tr>
<td>Ti-II to Ti-i-II</td>
<td>N/A</td>
<td>0.352 (3.22)</td>
<td>0.416 (2.42)</td>
<td>N/A</td>
</tr>
<tr>
<td>Ti-i-I to Ti-i-Ia</td>
<td>N/A</td>
<td>2.69</td>
<td>3.10</td>
<td>3.75</td>
</tr>
<tr>
<td>Ti-i-I to Ti-i-II</td>
<td>N/A</td>
<td>0.718 (0.763)</td>
<td>0.314 (0.408)</td>
<td>1.23 (0.973)</td>
</tr>
<tr>
<td>O-I to O-Ia</td>
<td>0.0043</td>
<td>0.801</td>
<td>0.844</td>
<td>0.286</td>
</tr>
<tr>
<td>O-I to O-II</td>
<td>N/A</td>
<td>N/A</td>
<td>3.14 (0.624)</td>
<td>0.900 (2.34)</td>
</tr>
<tr>
<td>O$_2$-I to O$_2$-Ia</td>
<td>N/A</td>
<td>N/A</td>
<td>0.627</td>
<td>0.127</td>
</tr>
<tr>
<td>2O-II+Ti-i-I to TiO$_2$-I</td>
<td>N/A</td>
<td>1.62 (2.94)</td>
<td>0.761 (3.16)</td>
<td>0.559 (4.73)</td>
</tr>
<tr>
<td>O$_2$-I+Ti-i-I to 2O-I+Ti-i-I</td>
<td>N/A</td>
<td>N/A</td>
<td>0.283 (1.92)</td>
<td>0.542 (2.38)</td>
</tr>
<tr>
<td>Ti-II to 2Ti-i-II</td>
<td>N/A</td>
<td>0.844 (3.55)</td>
<td>0.549 (2.18)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 6.3: Forward (Reverse) transition barriers in eV.

of a Ti-i-II interstitial without the vacancy, particularly when using the QEq potential. While the formation barrier using the QEq potential is higher than that of the MQEq model it is still readily accessible at the temperatures and time-scales being considered.

6.5.9 Barriers

The transition barriers have been summarised in Table 6.3 to allow for quick comparison between the empirical potentials and DFT where available.
6.6 Transition Prefactors

<table>
<thead>
<tr>
<th>Transition</th>
<th>Prefactor</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti Interstitial Formation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-II to Ti-i-II</td>
<td>$2.72 \times 10^{12}$</td>
<td>$1.95 \times 10^8$</td>
</tr>
<tr>
<td>Oxygen Diffusion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-I to O-I</td>
<td>$5.49 \times 10^{13}$</td>
<td>0.364</td>
</tr>
<tr>
<td>$O_2$-I to $O_2$-Ia</td>
<td>$1.36 \times 10^{14}$</td>
<td>3990</td>
</tr>
<tr>
<td>$O_2$ Disassociation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2$-I+Ti-i-I to 2O-I+Ti-i-I</td>
<td>$1.60 \times 10^{16}$</td>
<td>$2.82 \times 10^{11}$</td>
</tr>
<tr>
<td>Ti Interstitial Anneals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2O-II+Ti-i-I to Ti$O_2$-I</td>
<td>$1.15 \times 10^{13}$</td>
<td>1.89</td>
</tr>
</tbody>
</table>

Table 6.4: Prefactors and rates for various significant transitions within the TiO$_2$ growth process using the MQEq potential.

The prefactor of the Hessian matrix has been calculated numerically for the atoms that were displaced the most between the transition origin and saddle point. Table 6.4 demonstrates the proposed model for TiO$_2$ crystal growth along with the associated prefactors and transition rates using the MQEq potential. It was previously described that considering the allowance for local temperature spiking due to the energy of the incident clusters a transition with a barrier lower than 1 eV should be accessible at the time-frames and temperatures being considered corresponding to a frequency of $1.59 \times 10^{-4}$ Hz thus all the described transitions are readily accessible at 300 K. The prefactor for the $O_2$ disassociation is unnaturally high suggesting that the potential energy landscape of the minimum is very flat compared to that of the saddle point and that perhaps the transition does not obey hTST [32], which requires that the minimum basin can be described by a function of quadratic form while the transition saddle point can be described by a function of parabolic form. Despite the high $O_2$ disassociation prefactor the majority of the prefactors are close to the assumed value of $10^{13}$ meaning it is the exponential component of the Eyring equation that determines the probabilistic ordering of the transitions rather than the prefactor.

6.6.1 Conclusions

All three empirical potentials provide a reasonable approximation of TiO$_2$ behaviour when benchmarked against DFT results and experimental data where available. Most barriers are relatively high indicating that surface transitions for most ad-atoms will occur with a frequency lower than the incidence of additional ad-units. However both variable charge potentials indicate that Ti interstitials will form readily suggesting that many incident clusters will produce Ti interstitials even at low deposition...
energies. Given the high probability of Ti interstitial formation and the low relative immobility of most ad-atoms it not immediately apparent how further rutile crystal growth could be achieved, considering that all Ti ad-atom binding sites are equivalent to future interstitial locations. However DFT data indicates that the O-I ad-atom and O$_2$-I ad-molecule will be highly mobile and combined with a low Ti interstitial escape barrier in the region of oxygen ad-atoms we obtain a conceivable mechanism for crystal growth: Incident Ti$_x$O$_y$ units result in the production of oxygen ad-atoms and Ti interstitials. Oxygen ad-atoms and O$_2$ ad-molecules diffuse rapidly until they are in the neighbourhood of Ti interstitials. The interstitials can then escape, preferably through a relatively low energy exchange mechanism to form a TiO$_2$ unit within the trench. As the Ti ad-atom within the ‘upper hollow’ is equivalent to a future interstitial location it is necessary for this process to repeat itself as further layers form. This proposed mechanism for TiO$_2$ crystal growth has been somewhat validated through variable-temperature STM observations, showing that the rutile (1 1 0) surface grows by combination of gas-phase oxygen with mobile interstitial Ti ions from the bulk [12].

If the DFT results are representative of the true TiO$_2$ rutile surface behaviour then it is clear that modelling growth using the fixed charge potential will provide little insight into the correct growth dynamics during the industrial process due to the inability to account for Ti interstitials, combined with a poor representation of the oxygen binding sites. However, the fixed charge potential was not designed for modelling non-stoichiometric systems and when dealing with charge neutral systems such as the case of the TiO$_2$ ad-cluster the barriers produced are in surprisingly good agreement with DFT data. While the original QEq method has the potential to reproduce the correct behaviour due to the ability to capture most of the crucial binding sites, the large Ti interstitial escape barrier coupled with the slow oxygen diffusion rate indicate that were growth modelled at industrial temperatures and deposition rates, the growth would be highly defective containing an exaggerated number of Ti interstitials and perhaps forming amorphous TiO$_2$ once beyond the initial first layers of growth.

The modified QEq model has the potential to produce crystalline TiO$_2$ growth using the highly diffusive O$_2$ ad-molecule coupled with Ti interstitial annealing method that DFT results seem to suggest. Crucially the increase in hardness has dropped the Ti interstitial escape barrier to a readily accessible frequency within the time scales being considered, rendering it likely that the Ti interstitial will anneal in the region of oxygen ad-atoms well before a secondary deposition occurs. While the introduced O$_2$ ad-molecule fails to reproduce the extremely low transition barrier observed using DFT,
it is still the most rapid means of diffusion for the oxygen ad-atoms and once again available within the time-scales being considered. Unfortunately, due to the heightened interstitial escape barrier combined with the slower oxygen diffusion, it is likely that the number of Ti interstitials observed when modelling rutile growth using the MQEq potential will be exaggerated compared to equivalent DFT behaviour, however it is hoped that the dynamics are close enough to the correct behaviour that the formation of successive rutile like layers will be possible even if those layers are highly defective.
Chapter 7

Single Molecule Deposition

In order to gain insight into the typical defect structures that might occur during the growth of rutile, single Ti$_x$O$_y$ clusters were deposited onto the rutile (1 1 0) surface and the results were analysed. Clusters were deposited with kinetic energies corresponding to those typical of the industrial process at 10, 20, 30 and 40 eV [91]. The clusters were initialised 5 Å above the lattice surface and deposited normal to the surface with the orientation of the cluster randomised.

The substrate consisted of 1152 atoms arranged in a slab that was 6 layers deep providing a surface area of 24.43 Å by 26.93 Å. The surface was decomposed into the smallest symmetrically irreducible area and clusters were deposited within an aperture between (10.67, 9.14) and (14.75, 11.41) angstroms as shown in Figure 7.1.

![Figure 7.1: Irreducible surface area on TiO$_2$ rutile (1 1 0) surface.](image)

The size of the surface was large enough to contain all defects produced through deposition without the use of periodic boundary conditions, so fixed boundaries were used with DPMTA for computational efficiency. Energy was removed from the substrate after each deposition using a thermal
layer of atoms linked to a Berendsden thermostat.

In order to acquire good statistical averaging every combination of cluster and energy was repeated 1000 times with each deposition initiated randomly within the reduced area. The clusters deposited were Ti, TiO, TiO$_2$, O and O$_2$.

7.1 Defect Analysis

It is relatively straightforward to analyse a defective lattice to ascertain the number of interstitial, vacancies, ad-atoms and reflected atoms that have been formed. Using a perfect reference lattice, valid atomic sites are compared to the defective lattice to find interstitials and vacancies. Vacancies are defined as original lattice sites which do not contain an atom within 1 Å. The Ti atoms within the reference lattice are binned according to height into a histogram which is used to ascertain the interlayer separation for the categorisation of Ti interstitials. Various attributes were found for each lattice, such as the number of each type of defect, the peak penetration depth of the interstitials and the degree of damage, where damage is taken to be the sum of interstitials and vacancies, i.e. defects that perturb the perfect lattice.

7.1.1 Ti Deposition

10 eV

Table 7.1 shows the average number of interstitials, ad-atoms, reflected atoms and vacancies for a 1000 depositions of Ti at 10 eV. Considering that only a single Ti is being deposited, it is interesting to note that the statistical average for interstitial formation is greater than one. Having observed the small barrier for direct interstitial formation in the previous chapter, it might be expected that the majority of the interstitials are formed directly; however this is clearly not the case with 71.2% of the interstitials being formed via an exchange or displacement process. Despite the high probability of interstitial formation, some proportion of Ti atoms relax on the lattice surface such that the ratio of Ti to oxygen ad-atoms is almost even. Given that the percentage of ad-atoms that are formed directly correlates with the ratio of ad-atoms that are Ti, it is clear that all the Ti ad-atoms were formed directly with no internal Ti atoms being drawn onto the surface at 10 eV. The low average number of ad-atoms and high average number of interstitials indicates that the majority of vacancies are formed.
via Ti surface atoms being knocked into interstitial locations, which the high ratio of Ti to oxygen vacancies confirms. No atoms are ejected, where ejection can occur via reflection or sputtering. The average peak penetration depth for each deposition correlated to a first layer Ti interstitial while the absolute peak penetration depth corresponded to a 2nd layer Ti interstitial relaxation site. The average amount of damage per deposition was 2.054 while the peak damage factor was 5, where the damage factor is a measure of the number of interstitials plus vacancies.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.423</td>
<td>1/0</td>
<td>28.8</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>0.208</td>
<td>0.438/0.563</td>
<td>43.3</td>
</tr>
<tr>
<td>Ejected</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.631</td>
<td>0.813/0.187</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.1: The average number of defects produced during 1000 depositions of Ti at an energy of 10 eV.

Figure 7.2 shows a schematic of the irreducible surface area within which all the depositions occurred. The scatter plot overlaid on the schematic demonstrates the degree of damage caused as a function of Ti incidence. The colour and size of the dots indicates the degree of damage the was cause by the impact incident on that point.

Figure 7.2: Scatter plot of magnitude of damage from Ti deposition at 10 eV as a function of incidence.
The impact region resulting in the most damage appears to be that adjacent to the ad-row oxygen where a large number of depositions resulted in 4 defects. A typical example of one of these depositions is as follows; the Ti clips the edge of the oxygen ad-atom and creates an O-I vacancy and O-I ad-atom, the Ti ricochets into the 5-fold co-ordinated Ti creating a Ti-I vacancy with 2 Ti-i-II interstitials - producing a total damage factor of 4. Once an oxygen atom from the ad-row has been displaced, it seems that the formation of the of a Ti-i-II interstitial from the 6-fold Ti is energetically accessible as this formation sequence was seen on several occasions. The most common cause of 3 defects is the formation of a Ti-i-II split interstitial and a 5-fold Ti vacancy. It seems the window for creating the peak damage factor of 5 defects is small with it only occurring when the Ti strikes the centre of the surface oxygen atom, with depositions less than a tenth of an angstrom away from the centre producing only 3 defects at most. After the Ti ad-atom strikes the surface oxygen the oxygen atom pushes the ad-row Ti into a Ti-i-I interstitial location while the Ti ad-atom goes on to form yet another Ti-i-II split interstitial - corresponding to 2 vacancies + 3 interstitials = 5 defects.

Figure 7.3: Second layer Ti interstitial formed via double exchange mechanism.

Figure 7.3 demonstrates the formation of a second layer interstitial via a double exchange
mechanism, the Ti atoms are coloured gold so that the trace of movement is easy to distinguish. The depositing Ti atom strikes the 6-fold Ti which in turn exchanges with a 2nd layer Ti atom in order to form a 2nd layer interstitial. The deposition also results in the exchange of the 2 surface oxygen atoms to the right of the 6-fold Ti although no damage is caused.

20 eV

Doubling the energy from 10 to 20 eV produces a nearly linear corresponding increase in peak damage factor, rising from 5 to 9 defects, however, the average damage does not behave similarly increasing by only 21% to 2.488. Both the peak penetration depth and the average interstitial depth have not changed from the 10 eV depositions at layers 2 and 1 respectively.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.629</td>
<td>0.996/0.0043</td>
<td>29.5</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>0.23</td>
<td>0.326/0.674</td>
<td>32.2</td>
</tr>
<tr>
<td>Ejected</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.859</td>
<td>0.811/0.189</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.2: The average number of defects produced during 1000 depositions of Ti at an energy of 20 eV.

As might be expected the number of interstitials has increased in Table 7.2, with the proportion of those interstitials that were formed directly from the incident Ti remaining very close to the value at 10 eV. While the number of ad-atoms has increased marginally, the number that are formed directly from the incident Ti has actually decreased; suggesting that the ad-atoms will be predominantly oxygen atoms, something the Ti/O ad-atom ratio confirms. This indicates that the Ti atom is able to penetrate the lattice surface more frequently at a higher energy. The number of vacancies increases by 36%, however the proportion of vacancies that are composed of Ti and O remain the same. As at 10 eV there is still not enough energy to reflect the incident Ti or sputter any of the substrate.

In contrast with the damage plot at 10 eV, Figure 7.4 demonstrates somewhat homogenous lattice damage as a function of incidence point. Collisions with the side of the ad-row oxygen produce the same damage factor of 3 despite the increase in deposition energy. Close to the centre of the surface oxygen atom there is a similar peak to that seen at 10 eV, however, with a larger radius of damage, peaking at 8 defects. The peak damage occurs in the region between the two surface oxygen atoms in the centre of the trench, where a low damage factor was found for 10 eV impacts.
30 eV

In Table 7.3 there is a small increase in the number of interstitials found at 30 eV relative to those at 20 eV, while the proportion of those that are formed directly remains almost constant. At 30 eV we have just crossed the threshold where the majority of deposited Ti atoms finish in interstitial locations - with the remaining 42% mostly falling into valid Ti sites via an exchange mechanism and less than 4% forming ad-atoms. As with the previous 2 energies, no Ti is able to penetrate beyond the 2nd layer whilst the majority of interstitials finish in the first layer. The peak damage achieved has actually dropped from 20 eV at 8 defects, while the average damage has jumped to 3.013. There is enough energy to cause the ejection of oxygen atoms, although the event is extremely infrequent occurring in just 0.2% of depositions.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.799</td>
<td>0.998/0.0016</td>
<td>32.4</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>0.413</td>
<td>0.123/0.877</td>
<td>9.44</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.002</td>
<td>0/1</td>
<td>0</td>
</tr>
<tr>
<td>Vacancies</td>
<td>1.214</td>
<td>0.697/0.303</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.3: The average number of defects produced during 1000 depositions of Ti at an energy of 30 eV.
A high average damage and low peak damage suggests the scatter plot of the damage as a function of incidence will be even more homogeneous than seen at 20 eV.

![Figure 7.5: Scatter plot of magnitude of damage from Ti deposition at 30 eV as a function of incidence.](image)

As the energy has increased the regions of peak damage have become broader and less defined in Figure 7.5. As seen previously impacts at the side of the ad-row oxygen produce high degrees of damage along with impacts on the bridge between the surface oxygen atoms. New at 30 eV is the formation of large degrees of damage when the Ti atom is incident between the ad-row oxygen, the surface oxygen and the 6-fold Ti atoms, a site that corresponded to only low to medium levels of damage previously.

**40 eV**

While the number of interstitials increases once again at 40 eV the proportional change in interstitial numbers is less as we increase the deposition energy, shown in Table 7.4. At 40 eV a single interstitial was able to form at the 4th layer, however, surprisingly this is not a Ti interstitial; an anomalous O\(_2\) split interstitial formed in the fourth layer as shown in Figure 7.6. This O\(_2\) relaxation site is extremely unstable and if formed close to the lattice surface will move to the surface during the simulation time. For the first time we see a change in the average Ti interstitial depth with most depositions
producing a Ti interstitial that relaxes in the second lattice layer. The peak damage increases to 11, while again there is a significant increase in average damage to 3.472. The vast majority of ad-atoms are now comprised of oxygen and once again the number of oxygen atoms that have been sputtered from the surface increases but the probability is still low at 1 sputtered atom per 200 depositions. The vacancies behave similarly to the previous cases with the total number formed increasing while the proportion of Ti vacancies decreases.

<table>
<thead>
<tr>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.91</td>
<td>0.997/0.0031</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>0.647</td>
<td>0.108/0.892</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.005</td>
<td>0/1</td>
</tr>
<tr>
<td>Vacancies</td>
<td>1.562</td>
<td>0.624/0.376</td>
</tr>
</tbody>
</table>

Table 7.4: The average number of defects produced during 1000 depositions of Ti at an energy of 40 eV.

The peak lattice damage in Figure 7.7 corresponds to atoms incident on the side of the ad-row oxygen atom. Broad peaks exist between the ad-row oxygen and the surface oxygen and between the surface oxygen and the 5-fold Ti, however, they are not clearly defined. Impacts directly on the 6-fold Ti atom seem to produce remarkably little damage compared to the rest of the region.
7.1.2 TiO Deposition

10 eV

Table 7.5 yields the lattice damage caused by the TiO depositions performed at 10 eV. The number of interstitials formed is low compared to the Ti results, however, the proportion of those interstitials that are formed directly is almost identical at 28.8% for Ti and 29.5% for TiO. As would be expected the number of ad-atoms is much larger due mainly to the incident ad-oxygen, however an unexpected number of Ti ad-atoms are also formed. While the number of directly formed ad-atoms has increased, the number of ad-atoms created indirectly has dropped compared to Ti at 10 eV. For the first time some atoms are reflected implying that it requires less energy to bounce an oxygen atom off the surface than to sputter atoms. In accordance with the drop in the proportion of indirectly formed ad-atoms the proportion of oxygen vacancies has dropped relative to Ti at 10 eV, while the overall average number of vacancies is very close to the value found using just Ti.

Much like the Ti results the average interstitial penetrated to the first layer while the peak interstitial penetration was to the second layer. Due to the abundance of ad-atoms the damage factor has decreased compared to the Ti results with an average damage of 1.685 and peak of 4 defects.

The distribution of damage across the lattice surface is shown in Figure 7.8. Unlike the map of
7.1. DEFECT ANALYSIS

CHAPTER 7. SINGLE MOLECULE DEPOSITION

<table>
<thead>
<tr>
<th>Defects</th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.065</td>
<td>1/0</td>
<td>29.5</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.551</td>
<td>0.339/0.661</td>
<td>97.2</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.002</td>
<td>0/1</td>
<td>100</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.62</td>
<td>0.953/0.046</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.5: The average number of defects produced during 1000 depositions of TiO at an energy of 10 eV.

Figure 7.8: Scatter plot of magnitude of damage from TiO deposition at 10 eV as a function of incidence.

For Ti at 10 eV, there are no clear impact sites that produce higher damage. This indicates that defect numbers are as much a function of cluster orientation as position of incidence. The only insights that can be drawn from this data is that impacts directly above the 6-fold Ti atom produce little damage regardless of orientation.

20 eV

Table 7.6 demonstrates that the number of interstitials formed increases compared to 10 eV while the proportion of those interstitials that were formed directly remains roughly constant as seen in the other cases. Much like the Ti results, the deepest interstitial is formed in the second layer while the average interstitial depth from each deposition is within the first layer. There is a large jump in
peak damage to 10 defects as we move from 10 to 20 eV while the change in average damage factor is small at only 1.898 defects per deposition. We see a drop in the numbers of ad-atoms as we increase the deposition energy. This is because of an increase in Ti interstitials rather than oxygen reflection. The number of reflected atoms is still very low with no sputtering while the number of vacancies has increased slightly compared to 10 eV.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.241</td>
<td>0.997/0.0032</td>
<td>29.4</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.407</td>
<td>0.236/0.764</td>
<td>84.4</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.007</td>
<td>0/1</td>
<td>100</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.657</td>
<td>0.865/0.135</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.6: The average number of defects produced during 1000 depositions of TiO at an energy of 10 eV.

As with the results at 10 eV the damage peaks shown in Figure 7.9 are not correlated spatially. At 20 eV we can conclude that the damage is once again as much a factor of the cluster orientation as the position of incidence, however it seems that as with the 10 eV depositions, there is a lower average level of damage for clusters that are incident directly on the surface oxygen, particularly on the side closest to the oxygen ad-row.
30 eV

It is predictable by this point that the number of interstitials will increase almost linearly while the proportion of Ti to oxygen defects remains almost constant as shown in Table 7.7. For the first time when depositing TiO, we get Ti interstitial penetration into the 4th lattice layer. This indicates interstitial penetration depth is more a function of ad-cluster momentum then kinetic energy, as we did not see penetration to the fourth layer from the higher energy 40 eV Ti depositions. However, the average interstitial penetration depth remains within the first layer. The average damage factor rises to 2.273 and the peak damage remains at 10 defects. Again there is a drop in the number of ad-atoms, although very small, with a corresponding decrease in the proportion formed from Ti - the vast majority of Ti atoms forming interstitials. While the number of reflected atoms is still very low, the relative increase from 20 eV is large and for the first time oxygen is sputtered from the surface.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.425</td>
<td>0.999/0.0014</td>
<td>32.8</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.395</td>
<td>0.190/0.810</td>
<td>65.9</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.024</td>
<td>0/1</td>
<td>91.7</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.848</td>
<td>0.809/0.191</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.7: The average number of defects produced during 1000 depositions of TiO at an energy of 30 eV.

As with the previous cases, Figure 7.10 demonstrates that the degree of damage created through impacting the surface is as dependent on the rotation of the cluster as the impact site. Much like the previous TiO depositions it seems that there is a lower average damage value for impacts on the 6-fold Ti atom.

40 eV

Table 7.8 shows that the proportion of Ti interstitials that are created directly at 40 eV remains constant as seen in all previous cases. The average amount of damage per deposition climbs slightly while the peak damage actually drops to 9 defects. The deepest interstitial penetration depth is the 4th layer. The growth in interstitial formation decreases once more supporting the idea that the interstitial formation plateaus as the interstitial locations around the irreducible area become saturated. There is a minor increase in ejected atoms but the proportion of sputtered to reflected remains roughly constant. As seen previously the number of vacancies increases while the proportion
Figure 7.10: Scatter plot of magnitude of damage from TiO deposition at 30 eV as a function of incidence.

of Ti vacancies decreases.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.574</td>
<td>0.996/0.0044</td>
<td>29.6</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.466</td>
<td>0.160/0.840</td>
<td>48.6</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.029</td>
<td>0/1</td>
<td>89.7</td>
</tr>
<tr>
<td>Vacancies</td>
<td>1.074</td>
<td>0.739/0.261</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.8: The average number of defects produced during 1000 depositions of TiO at an energy of 40 eV.

At 40 eV it is finally possible to draw some conclusions regarding the damage as a function of impact location within the irreducible surface area. Figure 7.11 shows that peak damage occurs most frequently when depositing between atoms, such as between the surface oxygen and the ad-row oxygen and between the 5-fold co-ordinated Ti and the surface oxygen. This pattern of behaviour correlates well with the Ti results at 40 eV.
7.1. DEFECT ANALYSIS

7.1.3 TiO$_2$ Deposition

10 eV

Table 7.9 gives the statistics for the 1000 depositions of TiO$_2$ at 10 eV. It is immediately apparent that at this energy TiO$_2$ barely perturbs the underlying substrate with the majority of depositions not producing interstitials and a bias towards indirect formation. Therefore it is unsurprising to find that the number of ad-atoms is almost exactly equal to the number of atoms being deposited implying that in many cases the ad-cluster will come to rest as a surface TiO$_2$ unit with little in the way of further defects. Despite occurring when depositing TiO at 10 eV, we see no reflection of oxygen when depositing TiO$_2$ due to the reduced kinetic energy of each oxygen atom. As most interstitials are formed from the original substrate Ti atoms it is no surprise to find that the number of vacancies is almost the same as the number of interstitials.

The conclusion that the majority of depositions result in a TiO$_2$ ad-cluster with few further defects is supported by the low average damage of 0.633 along with the peak damage of 3 defects. Unlike all previous cases, no Ti interstitial penetrates beyond the first lattice layer.

Figure 7.12 reveals that once again the deposition damage is as much a function of the cluster
Table 7.9: The average number of defects produced during 1000 depositions of TiO$_2$ at an energy of 10 eV.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0.351</td>
<td>1/0</td>
<td>17.4</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>2.961</td>
<td>0.325/0.675</td>
<td>97.9</td>
</tr>
<tr>
<td>Ejected</td>
<td>0</td>
<td>0/1</td>
<td>0</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.312</td>
<td>0.997/0.0032</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 7.12: Scatter plot of magnitude of damage from TiO$_2$ deposition at 10 eV as a function of incidence.

orientation as the impact site. There is a possible peak corresponding to the ad-row oxygen however it is not clearly defined at this energy.

20 eV

At 20 eV the average damage increases considerably from the value found at 10 eV, roughly doubling while the peak damage also undergoes a large increase. Table 7.10 shows the majority of the depositions will now result in a Ti interstitial unlike at 10 eV. The proportion of interstitials that are formed directly has doubled and is now inline with the results found using Ti and TiO. The number of ad-atoms is still high, however a larger proportion are oxygen indicating that there are fewer TiO$_2$ ad-clusters. A small number of oxygen atoms are reflected, however there are no sputtered atoms.
The relative increase in Ti vacancies due to interstitial formation and increase in oxygen vacancies due to oxygen ad-atoms is roughly the same - the ratio of Ti to oxygen in the vacancies remains similar to that at 10 eV.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0.756</td>
<td>1/0</td>
<td>30.7</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>2.7</td>
<td>0.268/0.732</td>
<td>90.1</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.021</td>
<td>0/1</td>
<td>100</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.483</td>
<td>0.971/0.029</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.10: The average number of defects produced during 1000 depositions of TiO\textsubscript{2} at an energy of 20 eV.

The damage caused within the lattice is more a function of impact point than cluster orientation as clear patterns are defined as shown in Figure 7.13. Figure 7.13 also shows that, as at 10 eV, the damage peaks when depositions connect with the ad-row oxygen. A secondary peak indicates that clusters impacting the surface oxygen atom will also produces peak damage. This does not occur 10 eV.
30 eV

The relative change in damage is much smaller when increasing from 20 to 30 eV while the absolute change in peak damage remains constant, at 1.61 and 7 defects respectively. The deepest interstitial penetration depth is within the 3rd layer. However, most interstitials still come to rest within the first layer. Table 7.11 shows the change in the average number of interstitials from 20 to 30 eV is lower than from 10 to 20 eV and the proportion of Ti interstitials that are formed directly is roughly 30%. The number of ad-atoms decreases once again along with the proportion of ad-atoms that are Ti while the number of reflected oxygen atoms barely changes. Once more the number of vacancies increases in an accelerating fashion and the proportion of Ti vacancies decays.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0.981</td>
<td>1/0</td>
<td>32.2</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>2.62</td>
<td>0.224/0.776</td>
<td>80.6</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.023</td>
<td>0/1</td>
<td>100</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.629</td>
<td>0.892/0.108</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.11: The average number of defects produced during 1000 depositions of TiO$_2$ at an energy of 30 eV.

Figure 7.14: Scatter plot of magnitude of damage from TiO$_2$ deposition at 30 eV as a function of incidence.

The regions of peak damage are not so clearly defined at 30 eV, however Figure 7.14 retains the
peak damage region towards the centre of the surface oxygen atom. A secondary peak seems to occur over the ad-row Ti but is not clearly defined.

40 eV

As seen with previous depositions, the increase in average damage is linear while the peak damage undergoes an increase to 11 defects. At 40 eV there is enough energy to push an interstitial into the 4th layer but the average peak interstitial depth per deposition is still within the first layer. Once again the partial saturation of interstitial locations in the region of the impact diminishes the increase in average interstitials with energy. The number of ad-atoms decreases by a small amount in Table 7.12, as does the Ti ad-atom proportion. The number of reflected atoms actually decreases and for the first time we also see sputtering, although the probability is extremely low. The number of vacancies jumps again with an increase in the proportion that are made up of oxygen atoms.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>1.195</td>
<td>0.997/0.0025</td>
<td>29.8</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>2.583</td>
<td>0.183/0.817</td>
<td>65.0</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.017</td>
<td>0/1</td>
<td>94.1</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.8</td>
<td>0.823/0.178</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.12: The average number of defects produced during 1000 depositions of TiO$_2$ at an energy of 40 eV.

Unlike the TiO depositions at 40 eV, Figure 7.15 does not demonstrate peak damage correlating to the region between atoms, although it is clear that impacts directly on the centre of the surface oxygen atom will produce lower than average damage counts. A peak region appears to occur between the surface oxygen, the ad-row oxygen and the 6-fold Ti atom, however it is not clearly defined.

7.1.4 Oxygen

10 eV

With no mechanism for direct interstitial formation it seems likely that the number of interstitials formed will be far lower than seen previously. Table 7.13 confirms this with the lowest interstitial formation probability seen so far. Despite this the average damage is only marginally less than when depositing TiO$_2$ at 10 eV and the peak damage is the same. With no direct interstitial formation mechanism we also find that no Ti interstitials are formed below the 1st lattice layer. It is interesting
to find that some of the ad-atoms are formed via the removal of a surface Ti atom, usually to form a TiO ad-unit. Additionally a significant number of the ad-atoms are formed indirectly from original lattice atoms, usually due to a displaced ad-row oxygen. The total average number of ad-atoms remains close to 1 due to a large probability of reflection compared to the other deposited clusters. It is expected that a large proportion of the vacancies are due to Ti as the only mechanism to form a Ti interstitial is indirectly. The average number of defects formed is lower than when depositing TiO₂ at 10 eV, at 0.478 defects, despite the relatively large KE of the oxygen atom.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0.155</td>
<td>1/0</td>
<td>0</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.008</td>
<td>0.080/0.920</td>
<td>66.4</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.129</td>
<td>0/1</td>
<td>100</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.323</td>
<td>0.724/0.276</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.13: The average number of defects produced during 1000 depositions of oxygen at an energy of 10 eV.

Figure 7.16 shows that the regions where the oxygen ad-atoms are able to cause damage to the substrate are extremely well defined compared to the other clusters. The peak damage occurs when the oxygen strikes the edge of the surface oxygen between the 5-fold Ti and the ad-row oxygen.
Additional, lower damage peaks occur between the surface and the ad-row oxygen atoms and closer to the centre of the ad-row oxygen.

**20 eV**

There is a significant increase in peak and average damage counts when moving from 10 to 20 eV depositing oxygen. The degree of damage is still very small with a peak factor of 6 and an average of 0.64 defects respectively. All attributes undergo small increases, particularly the number of vacancies and the number of interstitials, the two values of course being correlated. Curiously, despite the small increase in the number of ad-atoms in Table 7.14, the proportion of those that are comprised of the original defect has also increased. As the number of ejected atoms also increases this seems counter-intuitive, however, the additional ejected atoms are sputtered rather than reflected. With the increase in ad-atoms and the small portion of sputtered oxygen atoms, the relative proportion of oxygen vacancies changes accordingly. As at 10 eV the deepest and average interstitial formation depth is in the first layer.

The map of damage produced in Figure 7.17 for 20 eV oxygen depositions is not as clearly defined as seen at 10 eV but still shows clear defect regions where maximum damage occurs. Curiously, the
### Table 7.14: The average number of defects produced during 1000 depositions of oxygen at an energy of 20 eV.

<table>
<thead>
<tr>
<th>Interstitials</th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.204</td>
<td>0.971/0.029</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.085</td>
<td>0.060/0.939</td>
<td>39.7</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.132</td>
<td>0/1</td>
<td>97.0</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.436</td>
<td>0.562/0.438</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 7.17: Scatter plot of magnitude of damage from oxygen deposition at 20 eV as a function of incidence.

The upper edge of the irreducible area which indicated a higher than average defect region is actually a minimum at 20 eV. The peak damage regions seem to correlate to between the surface oxygen and the 5-fold Ti atom and the surface and ad-row oxygen ad-atoms.

#### 30 eV

Previously a single anomalous oxygen interstitial relaxation configuration within the 4th lattice layer was demonstrated, so it surprising to find a number of oxygen interstitials which have formed directly from the incident oxygen atom. This is due to the introduction of a previously unseen oxygen split vacancy shown in Figure 7.18. The split oxygen vacancy results in an oxygen interstitial bridging the two vacant oxygen sites. While this relaxation site is conceivable it is curious that it was not
seen in any previous depositions. As per the other results the peak interstitial formation is within
the first layer and the average and peak damage have increased significantly to 1.127 and 8 defects
respectively, as shown in Table 7.15. The number of oxygen atoms ejected from the substrate actually
decreases which again is surprising given previous behaviour, while the number of vacancies increases,
closely correlated with the increase in interstitials and the proportion of vacancies being almost even
between the two species.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0.333</td>
<td>0.973/0.027</td>
<td>0.601</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.376</td>
<td>0.070/0.930</td>
<td>23.1</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.087</td>
<td>0/1</td>
<td>81.6</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.794</td>
<td>0.518/0.482</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.15: The average number of defects producing during 1000 depositions of oxygen at an energy
of 30 eV.

The damage map shown in Figure 7.19 is less defined than at 10 and 20 eV but demonstrates
a clear peak damage region directly between the surface and ad-row oxygen atoms which partially
correlates with the results of the 20 eV depositions.

40 eV

The 40 eV oxygen deposition results shown in Table 7.16 continue to show the total number of
interstitials increasing along with the relative proportion that are directly formed from the incident
oxygen atom. The deepest interstitial is an oxygen split interstitial in the 4th layer, while the average
interstitial penetration depth remains within the first layer. The absolute proportion of oxygen interstitials that are formed has greatly increased from less than 3% at the previous 2 energies to nearly 20%. The peak and average damage have undergone another significant increase to 1.46 and 12 defects. While the number of ad-atoms has increased slightly the proportion of Ti to oxygen ad-atoms has remained more or less constant at all energies. It is interesting to note that the number of ejected atoms has decreased once again with a significant proportion now consisting of sputtered surface atoms. The number of vacancies increases and the proportion of Ti and oxygen atoms that become vacancies is roughly even.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0.463</td>
<td>0.816 / 0.184</td>
<td>2.38</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.493</td>
<td>0.069/0.931</td>
<td>12.8</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.042</td>
<td>0/1</td>
<td>71.4</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.997</td>
<td>0.481/0.519</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.16: The average number of defects produced during 1000 depositions of oxygen at an energy of 40 eV.

Even at 40 eV the peaks in lattice damage are still well defined in Figure 7.20. A clear peak is still defined at the bridge between the surface and ad-row oxygen atoms along with a secondary
7.1. DEFECT ANALYSIS

7.1.5 $\text{O}_2$

10 eV

Given the prevalence of Ti interstitials and their low formation barrier it was unexpected that no interstitials were formed when depositing $\text{O}_2$ at 10 eV, as shown in Table 7.17. This results in a low average damage of 0.092 and peak damage of 2 defects. Nearly all depositions result in the $\text{O}_2$ relaxing as an $\text{O}_2$ ad-molecule on the surface or as 2 ad-oxygen atoms relaxing above 5-fold Ti atoms. The lack of formation of interstitials is easier to comprehend when considering the significant proportion of ad-atoms that are comprised of surface Ti ad-atoms. In the previous chapter it was shown that Ti interstitials in the presence of oxygen ad-atoms have a low barrier for the formation of TiO$_2$ which is also far more energetically favourable than the Ti interstitial on its own. It seems likely that any atom that would have become a Ti interstitial is drawn onto the surface. A reasonable proportion of oxygen atoms are reflected, although lower than seen at 10 eV when depositing oxygen atoms. The
vacancies are comprised almost entirely of Ti atoms pulled out of the surface rather than oxygen ad-row atoms that have been displaced.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.997</td>
<td>0.046/0.954</td>
<td>90.7</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.074</td>
<td>0/1</td>
<td>100</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.092</td>
<td>0.989/0.010</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.17: The average number of defects produced during 1000 depositions of O$_2$ at an energy of 10 eV.

Due to the overall lack of damage caused by the impacts, there is little discernible information yielded by the map of damage on the irreducible region shown in Figure 7.21.

Figure 7.21: Scatter plot of magnitude of damage from O$_2$ deposition at 10 eV as a function of incidence.

Due to the overall lack of damage caused by the impacts, there is little discernible information yielded by the map of damage on the irreducible region shown in Figure 7.21.

20 eV

The results of depositing O$_2$ at 20 eV are much like those at 10 eV with far fewer defects created on average than when depositing other clusters, as demonstrated in Table 7.18. Like the oxygen deposition at 20 eV there is a large disparity between the average damage and peak damage of 0.313 and 5 defects. At 20 eV we see a small number of interstitials are formed of which (11%) are oxygen atoms.
interstitials. The decrease in ad-atoms from 10 eV is perfectly accounted for by an increase in ejected
atoms with only a small amount of sputtering. We find the peak interstitial penetration depth is
within the 3rd layer; this defect is manifested in the form of another oxygen split interstitial which
is extremely unstable and anneals at a low temperature. The average peak interstitial depth per
deposition is within the first layer as would be expected.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0.094</td>
<td>0.883/0.117</td>
<td>0</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>1.731</td>
<td>0.053/0.946</td>
<td>73.2</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.342</td>
<td>0/1</td>
<td>99.4</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.219</td>
<td>0.785/0.215</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.18: The average number of defects produced during 1000 depositions of O\(_2\) at an energy of 20
eV.

As seen with the previous depositions there is little detail in Figure 7.22, due to the low average
number of defects produced per deposition. Whether defects are correlated by region or orientation
remains to be seen.
7.1. DEFECT ANALYSIS

CHAPTER 7. SINGLE MOLECULE DEPOSITION

30 eV

At 30 eV we have crossed the energy threshold required to produce defects in the majority of depositions with an average damage factor of 0.675, although the peak damage barely changes at 6 defects. The deepest interstitial is a 3rd layer oxygen split interstitial while the average interstitial peak depth is still within the 1st layer. Although the number of interstitials has increased the proportion of oxygen interstitials is the same as at 10 eV. The number of ad-atoms has increased with almost all ad-atoms being oxygen atoms as seen previously. It is surprising to see in Table 7.19 that fewer atoms are reflected as we increase energy although this behaviour correlates well with the results for the single oxygen atom impacts.

<table>
<thead>
<tr>
<th></th>
<th>Total Defects</th>
<th>Ti/Oxygen Ratio</th>
<th>Directly Formed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitials</td>
<td>0.185</td>
<td>0.881/0.119</td>
<td>0</td>
</tr>
<tr>
<td>Ad-atoms</td>
<td>2.013</td>
<td>0.067/0.933</td>
<td>61.2</td>
</tr>
<tr>
<td>Ejected</td>
<td>0.267</td>
<td>0/1</td>
<td>91.4</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.49</td>
<td>0.592/0.408</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.19: The average number of defects produced during 1000 depositions of O\textsubscript{2} at an energy of 30 eV.

Figure 7.23: Scatter plot of magnitude of damage from O\textsubscript{2} deposition at 30 eV as a function of incidence.

Figure 7.23 reveals little in the way of correlated damage peaks indicating that once again damage
is as much a function of the cluster orientation as it is the incidence site. There is some evidence to suggest that collisions in the region between the ad-row oxygen and surface oxygen result in higher numbers of defects but the region is not well defined.

40 eV

At 40 eV the $\text{O}_2$ split interstitial is produced once again and remains stable within the 3rd lattice layer and corresponds to the peak penetration depth for an interstitial. Both the average damage and peak damage undergo small increases with $\text{O}_2$ deposition at 40 eV producing fewer defects than any other cluster type at the same energy, at 0.775 and 8 defects respectively. While the number of interstitials increases, the total number of oxygen interstitials has actually decreased. There is a small rise in the amount of ejected atoms with the proportion of reflected to sputtered atoms remaining fixed. The number of vacancies also increases in Table 7.20, with the ratio of Ti to oxygen once again remaining similar to that at 30 eV.

<table>
<thead>
<tr>
<th>Interstitials</th>
<th>Ejected</th>
<th>Vacancies</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.204</td>
<td>0.324</td>
<td>0.571</td>
</tr>
<tr>
<td>0.961/0.039</td>
<td>0/1</td>
<td>0.567/0.433</td>
</tr>
<tr>
<td>0</td>
<td>91.4</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 7.20: The average number of defects produced during 1000 depositions of $\text{O}_2$ at an energy of 40 eV.

Unlike with some of the other clusters there is no emergent correlated behaviour evident in Figure 7.24 as we increase energy. It is therefore likely that the number of defects formed through deposition is more a factor of $\text{O}_2$ orientation than it is the position of incidence within the irreducible surface area.

7.2 Defect Classification

With a total of 20,000 different impacts it becomes impossible to manually classify each defect. A methodology was required that could automatically classify unique defects and group together identical defect structures reducing the total set of configurations that need to be humanly analysed. After a deposition all defect atoms were identified through comparison to the perfect unperturbed substrate. Defect atoms resulting from a each deposition, along with their nearest neighbours, were
combined into groups based on their proximity using a recursive grouping algorithm. As such, impacts resulting in disparate defects could potentially produce 2 or more defect groups. The original method for classifying defect groups constructed the minimum cuboid required to encompass all defect atoms within the group and then calculated the density at the centre of each cuboid surface. However, this was found to achieve lower than 20% success rate with either a large amount of false positives or a poor defect grouping. The defect boxing method also failed to cope well with rotational symmetry.

‘nauty’ (no automorphisms, yes?) is a program for determining the automorphism group of a vertex-coloured graph [64]. Through representing the defect cluster as a network graph nauty can assign a unique hexadecimal key that allows the classification and grouping of isomorphic graphs, i.e. 2 symmetrically equivalent defects produce identical hexadecimal keys.

The concept of a graph in this context is extremely simple; an atom is a vertex and the bond between atoms is an edge. An edge is created between atoms if the separation is less than the cut-off where the cut-offs for TiO are: Ti-Ti = 3.4, Ti-O = 3 and O-O = 3.75 Å in the rutile lattice and were determined from the radial density functions for the respective species. The vertices are coloured based on the species and hence in most cases the graphs will be partitioned into 2, as they will contain both Ti and oxygen atoms. Whilst this basic representation of the atomic co-ordination seems
simplistic, extensive testing yielded no false positives, i.e. no two different defects were identified as the same.

7.2.1 Example Defect

Consider a TiO-I ad-cluster as shown in Figure 7.25. The two ad-atoms have been included in the defect group along with some neighbours within the original substrate. Using the cut-off distances given previously a bi-coloured defect graph is constructed, which has been visualised using GraphViz [37] and is shown in Figure 7.26.

Reflecting the defect as shown in Figure 7.27 results in the production of an entirely different defect graph as demonstrated in Figure 7.28, however, crucially the 2 graphs are isomorphically equivalent. As such, when the graphs are analysed by ‘nauty’ they produce identical hexadecimal signatures, [73e6c 2a5a4a9 6852252]; hence we have an automated and rotationally invariant means of classifying defects.

7.2.2 Deposition Results

Using nauty to automatically classify defects resulted in 3450 unique hexadecimal keys corresponding to 3450 symmetrically unique defects. As the deposition energy increases it becomes more difficult to formally classify the resultant lattice, with large numbers of defects and degrees of lattice distortion resulting in a far higher incidence of unique defect lattices. For 1000 depositions per cluster there were a total of 5000 depositions performed at 10 eV producing 5366 separate defect clusters. The total number of clusters produced exceeds the number of depositions as many depositions will produce 2 sets of defects far enough apart to be classified individually. Of those 5366 clusters, 492 were unique at 10 eV while at 40 eV there were a total of 6014 defect clusters of which 1740 were unique.

With 20,000 depositions producing 22,948 defect clusters of which 3,349 were unique some descriptive analysis of the clusters was essential. While 3,349 defects were unique, the top 10 unique defects described 32% of the total configurations.
Figure 7.25: The TiO-I defect, including only defect ad-atoms and nearest neighbour atoms.

Figure 7.26: TiO-I defect graph defining the relationship between atoms within the defect. Produced using previously defined edge cut-offs and visualised using GraphViz. Ti represents titanium atoms and O\textsubscript{2} oxygen atoms.

Figure 7.27: TiO-I Defect reflected through the (001) plane.

Figure 7.28: Reflected defect graph.
Top 10 Defect Structures

**Defect 1 - 7.04% - O-I.** Figure 6.13. It is unsurprising that the single most common defect structure was the formation of a single oxygen ad-atom which occurred in 1616 cases, the vast majority of which are from the oxygen and $O_2$ deposition results.

**Defect 2 - 5.23% Ti-i-I.** The barrier calculations indicated that the formation of Ti interstitials would be highly likely and the statistical analysis confirms this. One possible surprise is that it is a Ti-i-I interstitial which is higher in energy and has a greater formation barrier than Ti-i-II.

**Defect 3 - 4.48% TiO$_2$-I.** Figure 6.5. Dominated by the TiO$_2$ depositions, the TiO$_2$-I defect commonly occurs, particularly at low energy.

**Defect 4 - 3.42% Ti-i-II split interstitial.** Figure 7.29 It was a little unexpected to find the Ti-i-I defect was the most common Ti interstitial, however, this defect cluster indicates that the total number of Ti-i-II interstitials will be greater but will most commonly occur in pairs.

Figure 7.29: The Ti-i-II split interstitial occurs in 3.42% of depositions.

Figure 7.29 shows an example of one of the Ti-i-II split interstitial defects produced after a deposition. The asymmetry of the Ti interstitials is typical with the Ti-i-II interstitial location consisting of 2 metastable configurations differentiated by height within the interstitial site.

**Defect 5 - 2.38% Ti-i-II split interstitial + O-I ad-atom.** Figure 7.30 A simple combination of 2 previously seen defects, 546 clusters consisted of an oxygen ad-atom which has come to rest over a Ti-i-II split interstitial pair.

**Defect 6 - 2.30% Ejected oxygen atom.** While the total number of ejected oxygen atoms remained low as a category compared to ad-atoms, interstitials and vacancies, as a unique defect it
7.2. DEFECT CLASSIFICATION

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Figure 7.30: The Ti-i-II split interstitial is often caused by an incident O atom which comes to rest above the interstitials.

occurs frequently.

**Defect 7 - 1.512% TiO-I ad-unit.** Figure 6.9. Yet another defect that is more prevalent at low energies, the TiO-I ad-atom was formed in 347 cases, primarily directly from TiO and TiO$_2$ depositions, however with a surprisingly large proportion from low energy oxygen depositions.

**Defect 8 - 1.31% O-II vacancy + Ti-II Vacancy + Ti-i-II Interstitial.** The first complex defect this occurs with a high frequency. An oxygen atom is removed from the surface leaving an O-II vacancy. Due to the missing oxygen bond the Ti-II atom moves into the Ti-i-II interstitial location leaving a Ti-II vacancy.

**Defect 9 - 1.25% Ti-i-I interstitial.** The first false classification is due to the multiple metastable relaxation points within an interstitial site. An effectively identical Ti-i-I defect results in a different defect graph and hence is classified as unique.

**Defect 10 - 1.22% O-I Vacancy + 2×Ti-II Vacancy + O-I Ad-atom + 2×Ti-i-II interstitial.** Figure 7.31. This complex structure occurred with a high frequency. The formation of the defect was not evenly distributed throughout all deposition results, with most instances occurring during the single oxygen depositions.
Figure 7.31: A complex defect; an oxygen atom has been knocked from the ad-row while an oxygen ad-atom has relaxed over a 5-fold Ti and a Ti-i-II interstitial. On the other side of the O ad-row the 5-fold Ti has been knocked into a Ti-i-II interstitial location.

7.2.3 Conclusions

In the previous chapter it was concluded that the low Ti interstitial formation barrier would likely result in large numbers of interstitials during rutile growth. The single molecule deposition statistics further validate this with high numbers of interstitials being produced even at low energies. This is particularly evident when depositing single Ti atoms, as shown in Figure 7.32(a). When depositing Ti and TiO the chance of forming an interstitial is high. When depositing Ti it is surprising to see that the probability of forming 2 interstitials is greater than the probability of forming no interstitials despite the low interstitial formation energy, as at least one interstitial must be formed from a surface Ti with a corresponding high defect formation barrier.

Figure 7.32: Number of interstitials produced for every cluster type at 10 and 40 eV.

At 40 eV the probability of forming interstitials, shown in Figure 7.32, is high with a single deposition of Ti, TiO and TiO$_2$ producing up to 5 interstitials and low probabilities of not deforming the original substrate. Despite the large number of interstitials formed at 40 eV, for most species it
was found that as the deposition energy increased the growth in the number of interstitials formed began to plateau. A likely explanation for this is that there are a limited number of valid interstitial relaxation sites which start to become saturated with displaced Ti substrate atoms as the energy is increased.

![Figure 7.33: Peak TiO interstitial depth as a function of energy.](image)

While the formation of large numbers of stable interstitials might be conducive to defective lattice growth it is likely that interstitial penetration depth will play a larger role in residual lattice deformation. Figure 7.33 demonstrates that at 10 eV in addition to the low numbers of interstitials very few Ti atoms are able penetrate the substrate beyond the 1st lattice layer. The numbers of interstitials penetrating to the 2nd layer are similar at 20 and 30 eV and remain low however at 40 eV we appear to have passed a critical point that allows a relatively large number of 2nd layer defects, this is likely due to the partial saturation of 1st layer interstitial locations in addition to the accessibility of higher energy transitions. With Figure 7.34 demonstrating that greater than 10% of TiO depositions producing interstitials in the 2nd layer below the surface at 40 eV it is highly likely growth will produce highly defective rutile as the deep Ti interstitials will be more difficult to anneal; the primary concern being that rate at which 2nd layer interstitials anneal will be slower then the rate at which they are produced at 40 eV. It seems that for perfect crystal growth when depositing individual Ti and TiO clusters, along with O and O₂, a deposition energy of 20 eV or lower would provide optimum growth.

TiO₂ depositions fair little better at 40 eV with nearly 10% of depositions once again producing interstitials within the second layer. Depositions at 20 eV are markedly different with very few
depositions producing interstitials below the first lattice layer and a high chance of defects annealing within the growth time-scales.

One unexpected emergent attribute was the relationship between the total number of interstitials and the number of interstitials that were formed by the impact species directly. For almost all depositions of clusters containing Ti atoms, particularly at higher energies, the ratio remains close to 30% with very little deviation.

While in most cases it is safe to assume that the defect attributes such as numbers of interstitials and vacancies increase with energy, this is not always the case. An easily understandable example is that the numbers of ad-atoms found when depositing TiO and TiO$_2$ decrease at higher energies as shown in Figure 7.35. As the deposition energy increases the clusters are more able to break their bonds such that the Ti can directly form an interstitial and the oxygen atoms can reflect off the surface more easily. Less easy to understand is that the number of oxygen atoms reflected from the surface decreased for oxygen and O$_2$ when depositing at 30 eV compared to 20 eV.

The scatter plots of damage provide some insight into likely critical defect formation points, with the centre of the surface oxygen atom, the 6-fold Ti atom and the edge of the oxygen ad-row atom all producing high levels of damage for various combinations of defects and energies. There is, however, no global trend that emerges for all species. At low energies it is generally true to conclude that the orientation of molecular ad-units plays a strong role in the degree of defect production, particularly in the case of O$_2$ where no discernible damage peaks are ever defined.

In order to grow rutile with the least number of defects it would seem sensible to deposit
predominantly TiO$_2$ units at the lower end of the energy spectrum. Given second layer interstitials cannot directly anneal it seems likely that if depositing at 40 eV, the critical jump in 2nd layer interstitials will produce defective rutile or amorphous growth.

The analysis of the top 10 most common defects yielded few surprises with simple defects such as Ti interstitials and oxygen ad-atoms occurring with the highest frequency. However, given the complexity of the 10th most common defect, it is likely that messy defects with low formation energies will occur with a higher frequency then many of the simple binding configurations investigated in the previous chapter.
Chapter 8

Growth

It was indicated in the ‘Long Time-Scale Dynamics’ chapter that when modelling growth through sputter deposition it is likely that the realistic deposition rate for the system size being considered will be inaccessible on the MD time-scale and as such a standard MD simulation would not be able to model multilayer growth. A rough approximation of the correlation between computational real time and simulation time is approximately 1 fs simulated time per second of computational time. Given a small substrate of 432 atoms, comprising 4 layers and a surface area of approximately 0.4 nm$^2$ (shown in Figure 8.1), the expected flux rate during a typical growth process is roughly 10 TiO$_2$ units per second. To grow a single additional layer a minimum of 36 depositions are required, corresponding to a simulation time of 3.6 s, requiring approximately $10^{12}$ hours computational time which is clearly inaccessible.

![Figure 8.1: TiO$_2$ substrate containing 432 atoms in 4 layers.](image)
In order to allow for feasible simulation of growth one approach is to increase the deposition rate. The fastest rate at which depositions can be performed during a simulation, while preserving realistic deposition dynamics, is dictated by the time in which it takes for the excess energy to dissipate via atoms coupled to the Berensden thermostat. With the bottom layer of the lattice shown in Figure 8.1 fixed and the next 2 atomic layers coupled to a thermostat, the energy from a single deposition at 20eV is dissipated within approximately 4.5 ps. Allowing for a minimum of 100 depositions before multilayer growth can be accurately investigated this implies a computational run time of $\sim 120$ hours using the guideline provided above.

Previous simulations in this thesis relied on fixed boundaries in conjunction with DPMTA for electrostatic evaluation, however, when modelling growth it is necessary that ad-atoms are able to diffuse freely about the surface of the lattice and thus periodic boundaries are necessary. As such it is necessary to use the periodic Ewald method rather than DPMTA resulting in far more expensive electrostatic evaluation then in the previous simulations, thus growth simulations involving the small 432 atom system take weeks rather than days as might otherwise be expected.

8.1 Growth at 300 K

It is likely that the simulated behaviour of the TiO$_2$ growth at 300 K will provide a poor reflection of the behaviour during the industrial process due to the extremely high flux, leaving little time for the defects to anneal. Of particular concern is the Ti interstitial which has been shown to form readily and has an annihilation barrier of 0.761 eV, corresponding to an attempt frequency of 1.64 Hz at 300 K. While some Ti interstitials may be able to escape during the simulation due to local thermal spikes, resulting from the incident depositing clusters, it is probable that the majority of interstitials will be immobile relative to the deposition rate. This suggests that simulated growth at 300 K with such a high TiO$_2$ flux will produce a highly defective crystal or amorphous structure. However, despite the approximation introduced through increased flux it is still interesting to model growth as it is not clear that the potential is capable of naturally forming a rutile crystal structure.

The advantage of simulation over experimental work is the ease with which parameters can be readily changed in order to investigate their influence. In this case one such interesting parameter is the probabilistic compositions of the clusters that are incident on the surface. Previous research [8] suggested that a proportion of sputtered Ti oxidises in-flight before depositing on the substrate and
8.1. GROWTH AT 300 K

Due to the frequency of Ti interstitial formation, correlated with the relatively large escape barrier it seemed likely that growth at 20 eV would produce a more perfect crystal than at higher deposition energies. The initialisation of the deposition was performed in the same fashion as when investigating the single molecule depositions, with clusters randomly orientated and inserted above the lattice before deposition normal to the surface. Unlike the single molecule deposition the clusters are given energy according to a normal distribution with a standard deviation a tenth of the deposition energy, hence when depositing at 20 eV the standard deviation was 2 eV.

After depositing 200 clusters the rutile structure has been largely retained, however as predicted there are large numbers of interstitials, some of which can be seen in Figure 8.2. An additional 359 atoms have been deposited nearly doubling the lattice and forming 3 complete layers. Several oxygen atoms have reflected off the surface, however the final stoichiometry remains close to perfect with an O/Ti ratio of 2.01, the total system being over stoichiometric due to statistical artefacts.

Considering only the clearly defined first 6 layers, there are 21 Ti interstitials with 5 residual within the original substrate, providing an interstitial per layer average of 3.5. While the structure is stoichiometric the large numbers of Ti interstitials have resulted in an oxidised and amorphous like upper layer with a local stoichiometry of 2.6 encompassing the top 5 Å of the lattice. This suggests that if the growth simulation was continued it is possible that further crystal growth could not be sustained due to the formation of amorphous like layers.

Plotting the radial distribution function (RDF) of the grown layers compared to the perfect substrate allows for a quick quantification of the quality of grown rutile as shown in Figure 8.3.

Figure 8.3 demonstrates that the grown layers share the primary peaks with the perfect substrate,
8.2 Growth at 1000 K

however a large amount of damage has occurred causing the RDF to become less clearly defined. It is a great success of the potential that the rutile structure is able to naturally form in successive layers merely by depositing atoms on a rutile TiO$_2$ template and the attributes of the grown lattice correlated with expected behaviour predicted using results from the previous chapters.

Figure 8.4 shows the energy of the lattice as a function of deposition. The relative energy is calculated by taking the average energy of Ti and O in the perfect substrate, -2.465 and -9.845 eV respectively, and subtracting the appropriate amount for each atom deposited. If layers were to form perfectly it would be expected that a series of energetic hills would form, with layer completion bringing the total energy towards zero. As the growth at 300 K is highly defective we see a net increase during the course of the simulation, however the drop at deposition number 170 corresponds to near completion of 6th lattice layer, providing some degree of the expected behaviour.

8.2 Growth at 1000 K

In the previous example the flux was such that one deposition occurred every 5 ps, a relative increase in frequency from the industrial process of $2 \times 10^{11}$. The formation of highly defective growth was expected due to the immobility of the Ti interstitials relative to the deposition flux rate. A means of compensating for the increased flux is to proportionally scale the temperature of the lattice such that the relative attempt frequency of transitions is similar to the relative increase in flux. Many of
the critical diffusion processes, including the Ti interstitial annihilation, were close to 1 eV and so this was used at the reference barrier to ascertain the appropriate temperature scale. Assuming a fixed prefactor of $10^{13}$, supported in the previous chapters, along with a 1 eV transition barrier we obtain a change in attempt frequency from $1.59 \times 10^{-4}$ to $9.12 \times 10^{7}$, providing a relative increase of $5.7 \times 10^{11}$. The similar relative scaling should allow for diffusion behaviour that is closer to that of the industrial process compared to accelerated growth at 300 K.

### 8.2.1 20 eV

Once again the growth simulation was performed with depositions around 20 eV, however the lattice was now thermalised to 1000 K for 7 ps before starting.

Figure 8.5 shows the growth after 200 depositions of 20 eV at 1000 K. It is immediately apparent that better crystalline growth occurs to that seen at 300 K. The total number of Ti interstitials has dropped to 4, all within the original substrate where the fixed bottom layers may be influential, yielding an interstitial per layer value of 0.57. Once again the random nature of the cluster selection has resulted in an over stoichiometric lattice with a deposited O/Ti ratio of 2.08 with oxygen reflection providing a ratio of 2.07 within the grown structure.
8.2. GROWTH AT 1000 K

8.2.2 40 eV

Single molecule depositions at 40 eV formed substantial numbers of 2nd layer Ti interstitials when compared to the equivalent behaviour at 20 eV. It was therefore likely that growth at 40 eV would result in a far greater number of residual interstitials, unable to anneal before the formation of successive layers. As before the lattice was heated to 1000 K for 7 ps before initialising the depositions, however when depositing at 40 eV it was necessary to allow the lattice to cool for 7 ps to avoid overheating.

After depositing only 100 atoms large numbers of interstitials were found to have formed. Whilst the lattice crystal structure was superior to that seen when depositing 20 eV clusters at 300 K, the interstitial per layer value was greater than the 20 eV depositions at 1000 K at 0.8. Due to the increased oxygen reflection probability at 40 eV, the O/Ti ratio drops to 1.95 after only 100 deposition steps. Figure 8.6 shows the radial density functions for the resultant lattices when depositing at 20 and 40 eV with a substrate heated to 1000 K.

Having confirmed that growth when depositing at 40 eV results in poorer crystal formation then when depositing at 20 eV it was decided that 20 eV would perform the optimum basis for further investigation into the influence of cluster composition on rutile growth.
8.2.3 Stoichiometry

The influence of the stoichiometry of grown layers on the quality of rutile was investigated. While it was likely that an excess of Ti would result in highly defective and possibly amorphous growth, it was unclear what influence an oxygen excess would play on the overall crystallinity.

Ti Deficient

In order to ensure the grown layers were under stoichiometric with an excess of oxygen atoms relative to Ti atoms, the probability of cluster selection was modified to those given in column B of Table 8.1 providing an average O/Ti ratio of 2.31 for the depositing species. After 120 depositions the total resultant O/Ti ratio was just 2.1, while the ratio within the top 5 Å was 2.5, considerably above the ratio of the depositing species. The few numbers of Ti atoms results in an oxidisation of the surface which in turn increases the probability of oxygen reflection during subsequent depositions, thus the O/Ti ratio in the substrate is self-limiting. In addition, due to the saturation of the surface with oxygen ad-atoms any interstitials that were formed were quickly annealed thus resulting in almost perfect rutile growth.
Next the influence of oxygen deficiency was investigated. The cluster probabilities are given in column C of Table 8.1 corresponding to a probabilistic O/Ti ratio of 1.63. After just 100 depositions very poor rutile growth was evident, with 44 Ti interstitials residing within the first 6 layers, providing a very high interstitial/layer ratio of 7.3 with a number of sub-surface Ti vacancies also occurring for the first time. None of the deposited oxygen was reflected and hence the resultant O/Ti ratio of 1.65 was close to the average value of the depositing species.

The comparative RDF plots for the Ti and oxygen deficient growth simulations are shown in Figure 8.7 compared to that of the perfect substrate.

Due to the lack of Ti interstitials, the Ti deficient growth clearly results in better rutile crystallinity than oxygen deficient growth, with a probabilistic O/Ti ratio of 2.0 below the surface. This implies that an increased oxygen pressure during the industrial growth process should result in better crystal formation.

### 8.2.4 Cluster deposition versus single atom deposition

It has been shown in previous chapters that the incidence of individual atoms generally results in a greater degree of damage then when depositing complete TiO$_2$ clusters. In order to ascertain the role
that cluster size plays in the formation of the rutile crystal, two growth simulations were performed with small and large numbers of clusters compared to single atomic species.

Cluster Deposition

The probability of cluster selection in Table 8.1 column D was used to ensure a high probability of selection of complete TiO$_2$ and TiO units over individual Ti atoms. After 160 depositions the O/Ti ratio was 2.02 with no oxygen reflected. Having grown to 8 layers there were no residual Ti interstitials and the rutile crystallinity was excellent. As with the excess oxygen growth the entire crystal below the surface contained a perfect stoichiometry, thus correlating with the previously seen behaviour when depositing clusters in the single molecule deposition chapter. The RDF shown in Figure 8.8 demonstrates the excellent correlation with the original substrate.

Single Atom Deposition

The probability of cluster selection was modified to use those given in Table 8.1 column E, corresponding to large numbers of incident individual Ti atoms. Given the results from the single particle deposition analysis it was likely that in the early growth stages large numbers of Ti interstitials would form with the potential to form amorphous TiO$_2$ during later growth.
Due to the large proportion of individual oxygen and O\textsubscript{2} clusters there was a corresponding increase in oxygen reflection relative to the behaviour seen during mixed cluster deposition. Combined with a large degree of Ti interstitial formation there was a resultant poor O/Ti ratio of just 1.82 in the deposited film while the O/Ti ratio within the top 5 Å was 2.18. Within the first 6 lattice layers there were 31 Ti interstitials providing another very high interstitial/layer average value of 5.2 however no Ti vacancies were formed in contrast to the oxygen deficient growth. The large numbers of Ti interstitials combined with the loss of oxygen through reflection results in an interface that is more like a Magnéli phase \cite{6} then the rutile polymorph of TiO\textsubscript{2}. The poor crystallinity is also evident in the RDF shown in Figure 8.8.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8_8.png}
\caption{The radial density functions of growth at 1000 K with deposition of complete clusters versus individual atoms.}
\end{figure}

Figure 8.8 demonstrates the radial density function plots for the cluster based growth versus the individual atom deposition. It is immediately apparent that the structure grown using cluster deposition at 20 eV correlates far more closely with the perfect substrate then that grown through predominantly atomic individual impacts.
8.3 Rutile Growth Mechanisms

The previous data provides some insight into the quality of grown rutile when depositing under certain conditions and previous chapters give information regarding the behaviour of individual atoms and defects during the growth process. It now becomes possible to compare the predicted defect formation and diffusion behaviour to the growth data to ascertain the growth mechanisms that occur during the crystal formation process.

It has previously been argued that it is highly likely that the growth process will involve the formation of interstitial Ti atoms which are then annealed by the subsequent arrival of oxygen ad-atoms in the neighbourhood. While many interstitials are formed directly, the lowest interstitial anneal barrier involves an exchange where a Ti surface atom in the presence of oxygen is pushed on top of the surface and the interstitial occupies the original Ti site. By extending the idea of direct interstitial formation coupled with an exchange based anneal mechanism to growth we can suggest that it would be possible and even likely that some Ti atoms are able to move towards the surface as each subsequent layer forms.

Figure 8.9 demonstrates an original substrate atom that has climbed 1.5 layers during the course of the growth simulation, supporting the theorised growth mechanism.

Figure 8.9: Height of Ti atom 246 during a 20 eV deposition growth process at 300 K. The peak height is the height of the highest atom that is connected to the lattice surface.
Some further evidence of this suggested growth mechanism would be a large number of Ti atoms from the original substrate surface level that have been replaced by subsequently deposited Ti atoms. In the case of the growth of 20 eV depositions at 300 K, 44.4% of the original substrate Ti atoms are from newly deposited clusters. There are three evolutionary mechanisms available to a Ti atom within the lattice; occasionally the atom will be knocked into a lower site by an incident cluster as shown in Figure 8.12. More commonly the atom will go through a series of exchanges either replacing a lattice site Ti or being replaced until it is several layers above its original position, as shown in Figure 8.11. Most likely, once stable the Ti atom will occupy the same site throughout the course of the simulation as shown in Figure 8.10.

![Figure 8.10: A Ti atom remains stationary throughout the course of the simulation.](image-url)
Figure 8.11: An atom travels upwards between lattice and interstitial sites using an exchange mechanism.

Figure 8.12: A Ti atom is knocked back into a lattice site after escaping.
8.4 Amorphous Substrate

While it has been shown that the modified QEq potential is able to successfully grow rutile TiO$_2$ under certain constraints, this is with the bias of an underlying perfect rutile substrate. In order to ascertain whether or not the rutile growth was an artefact of the underlying substrate or the growth conditions, growth was simulated on an amorphous substrate. The amorphous-like stable structure was formed through heating the perfect rutile substrate to 6000 K for 7 picoseconds with no boundary conditions before annealing. Figure 8.13 shows the amorphous substrate used for growth simulations.

![Amorphous substrate produced through heating the rutile substrate to 6000 K for 7 ps with no boundary conditions.](image)

8.4.1 Mixed Deposition

Initially clusters were deposited using the mixed cluster probability in Table 8.1 column A at 20 eV with the lattice once again heated to 1000 K. After depositing 180 atoms at 1000 K there was very little change in crystal structure as shown in Figure 8.14 and a visual inspection yielded no signs of an emergent crystal structure throughout the growth simulation.

8.4.2 Cluster Deposition

As cluster based deposition was previously shown to form excellent rutile when depositing on a rutile substrate, the parameters in Table 8.1 column D were used once again to encourage rutile formation when depositing on the amorphous surface. However, as with the mixed cluster growth, after depositing 247 atoms no visual evidence for the formation of a crystalline layer was observed.
8.5 Anatase Growth

Anatase is another commonly formed polymorph of TiO$_2$ that can occur during the magnetron sputtering process and is used, for example, in self-cleaning glass. The MQEq potential is able to stably reproduce the anatase polymorph and so it proved a good candidate for growth modelling. Figure 8.16 shows the original substrate upon which depositions were performed.
8.5. ANATASE GROWTH

Figure 8.15: The radial density functions of growth the perfect and amorphous substrates compared to grown lattices when depositing mixed units and full clusters.

8.5.1 1000K

Initially the lattice was heated to 1000 K to provide the temperature based acceleration of defect diffusion that allowed the formation of defect free rutile, however, even before deposition occurred there was some degree of surface reconstruction. Two growth simulations were performed, one corresponding to the mixed cluster probability and the other corresponding to the full cluster probabilities given in Table 8.1 columns A and D respectively. Figure 8.17(a) compares the RDF of the deposited film using mixed cluster probability to that of the amorphous substrate discussed above and seems to suggest that the grown film is amorphous due to the strong similarity of the two RDF plots. Figure 8.17(b) demonstrates the difference in RDF plots between the original anatase substrate and the two sets of deposited layers. There is little difference in the RDF profiles but the lattice appears under visual inspection to have slightly improved crystal structure when depositing mixed clusters, in contrast to the behaviour seen when growing rutile. It is not yet clear if the amorphous nature of the growth is an artefact of the variable charge potential which might give an amorphous phase as energetically preferential compared to the anatase phase or if the amorphous structure of the grown layer is purely due to the deposition conditions.
8.5. ANATASE GROWTH

8.5.2 300 K

It has been shown that anatase has a tendency to reconstruct to form rutile at high temperatures [25, 22, 21]. It is possible the amorphous like state is due to the reconstruction of the TiO$_2$ which is incomplete due to the fixed bottom layer and results in an undefined crystal structure. As the mix of clusters in Table 8.1 column A was shown to possibly produce slightly improved crystallinity, the same mix was used to perform growth at 300 K with depositions at 5 and 1 eV. Unlike at 1000 K, when heated to 300 K the anatase substrate remained stable with no reconstruction.

Figure 8.18 shows the RDF plot of 200 depositions onto the perfect substrate at 5 eV and 1 eV. Unlike the rutile growth, both simulations have produced poor anatase crystallinity in the successively formed layers. Upon visual inspection the growth at 1 eV appears to have a better crystallinity than at 5 eV, however, this is not evident in the RDF plots. While the oxygen atoms appear to follow a crystal structure, the Ti atoms place haphazardly with more in interstitial sites then valid crystal locations. What the growth at 300K has demonstrated is that if modelling of the growth of anatase is to become possible it will be necessary to accelerate the dynamics without heating the lattice and causing reconstruction.
8.5. ANATASE GROWTH

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Figure 8.17: (a) RDF of an amorphous substrate compared to the film grown on an anatase substrate at a 20 eV deposition energy. (b) RDF of an anatase substrate and grown films at 20 eV according to the stoichiometries given in columns A and D of Table 8.1

Figure 8.18: The RDF plots of growth at 5eV and 1eV compared to the perfect anatase substrate.
8.6 On-the-fly KMC

As shown previously, through increasing the temperature of a substrate it is possible to increase the attempt frequency of a target diffusion barrier such that the scaling corresponds to the increase in deposition rate. This has worked quite well and has allowed simulation of rutile growth with few or no defects producing results which are similar to those that might be experimentally expected.

An unfortunate drawback of increasing temperature is that the attempt frequency is exponentially dependent on both the barrier and temperature and hence the change in attempt frequency is non-linear for all transitions. Consider for example two transitions, the formation of a Ti-i-I interstitial from a Ti-I ad-atom, with a barrier of 1.15 eV and the diffusion of an oxygen ad-atom along the surface with a barrier of 0.84 eV. The difference in energy of these two transitions is just 0.31 eV, however the relative change in attempt frequency when increasing temperature from 300 to 1000 K is $8.41 \times 10^9$ for the Ti diffusion and $3.34 \times 10^{13}$ for the oxygen diffusion. This means that oxygen diffusion is 3970 times more likely to occur relative to Ti-I formation at 1000 K when compared to transition rates at 300 K, thus the behaviour will be biased at artificially high temperatures. It was hoped that the use of the OTF-KMC method would allow realistic growth modelling while avoiding the temperature bias.

Performance Issues

The original parameters of the simulation of TiO$_2$ growth used the standard mix of cluster probabilities given in Table 8.1 column A, with a deposition energy of 20 eV. Rather than using the correct industrial deposition frequency of 10 Hz, the deposition frequency was increased to 50 Hz to decrease the total number of KMC steps that were required to simulate multilayer growth. If a deposition event was chosen, it was initialised in the same way as the standard growth modelling, with clusters randomly orientated and deposited according to a user defined set of probabilities for species and kinetic energy. As the first few clusters were deposited the number of potential transitions was few and the system was able to rapidly evolve at a rate much faster than achievable through standard molecular dynamics, however once the system reached a sufficient complexity, the time evolution dramatically slowed due to the presence of large numbers of very low energy barriers. Once the surface achieves sufficient complexity various transitions appear that are well under 0.1 eV, typically involving loosely bound oxygen atoms oscillating between 2 or more configurations. At 350 K the probability of a 0.1 eV
transition occurring is $4.36 \times 10^8$ times more likely than a deposition, thus the KMC becomes trapped simulating the same oscillating particles moving back and forth, losing the performance benefit over classical MD.

A simple solution is to allow the KMC to recognise that the state has been previously visited through comparison with all previously visited configurations, thus it is unnecessary to perform fresh transition searches and the algorithm can reuse the old data. Despite being implemented this does not provide satisfactory performance boost as the comparison with previous configurations is an operation of the order of seconds and $4.36 \times 10^8$ seconds is obviously unacceptable, not to mention the vast storage space required to store the corresponding state files. Normand Mousseau [28] proposed a solution for this problem when looking at vacancy diffusion in silicon. Utilising the idea of ‘tabu’ search blocking [38], Mousseau investigated the influence of blocking previously visited configurations and previously performed transitions on the evolution of the lattice by comparing the statistical behaviour with an unrestricted KMC simulation. It was found that whilst blocking specific configurations adversely effected the statistical attributes of the KMC, blocking specific transitions introduced little bias to the simulation.

The specifics of the transition blocking method employed in this project are as follows: A storage buffer, or memory kernel, of previously undergone transitions is created at the beginning of the KMC run. Once a transition has been selected it is added to the top of the buffer and the transition at the end of the buffer, if one exists, is removed. For this research project a buffer length of 10 transitions was used, hence the previous 10 transitions are inaccessible to the KMC simulation. If the system arrives in a configuration that was recently visited, the transition that was previously performed has its probability set to zero in the KMC roulette such that there is no chance of it being repeated.

The ‘tabu’ transition blocking method works well for some KMC simulations, such as the evolution of complex defects within a closed system, however when applied to growth modelling it merely acts as a stop-gap measure, extending the time-scale that can be simulated before the KMC once again becomes entrenched in low energy diffusion barriers. This is due to the fact that the number of low energy transitions that are available quickly exceeds the number of blocked transitions within the buffer, unless we start using an extremely large memory kernel and severely bias the simulation.

In order to feasibly model TiO$_2$ growth using the OTF-KMC within reasonable time-scales, it was necessary to make some further approximations that inevitably effect the accuracy of the simulation.
Modelling TiO\textsubscript{2} Growth with OTF-KMC

The first and most significant approximation that was made in order to ensure simulation of the growth of TiO\textsubscript{2} within reasonable time-scales, was the limit of 5 unique transitions per KMC step. Whilst this is acceptable for the early stages of the KMC simulation where few numbers of ad-atoms and defects are present, as the complexity of the simulation increases it is likely that some low energy transitions will be missed and therefore the estimated time evolution of the simulation will be inaccurate, if not the overall statistical behaviour.

Despite the limited numbers of unique transitions at each step, coupled with the ‘tabu’ blocking, the system rapidly becomes dominated by low energy transitions that inhibit the KMC, rendering it potentially less efficient than classical MD. The second approximation resolved this issue by blocking all transitions that were below 0.5 eV. This could potentially influence the lattice evolution to a serious degree and is only acceptable if those transitions below 0.5 eV are conducive to unproductive oscillations rather than meaningful defect diffusion. The value of 0.5 eV was selected as a compromise that allowed for rapid evolution of the lattice, while still readily containing the critical barriers that were found when performing transition searches for simple defects on the lattice surface. An additional consideration is that whilst extremely low transitions are inaccessible during the KMC stage, they can freely occur during the MD deposition stage.

The third approximation was the cluster selection. Loosely tethered oxygen atoms were found to be the primary source of low energy barriers, being able to vibrate between configurations at extremely high frequencies. In order to restrict the number of mobile oxygen atoms the probability of cluster selection was altered such that only complete TiO\textsubscript{2} units were deposited during the MD stages of the KMC.

Results

Using the above conditions it became possible to simulate multilayer growth of TiO\textsubscript{2} through OTF-KMC for the first time. Figure 8.19 shows the lattice configuration after 130 KMC steps.

Through increasing the deposition frequency of TiO\textsubscript{2} to 50 units per second the probability of a deposition occurring became similar to a transition of 0.785 eV being selected at 350 K. This small transition barrier window of 0.5-0.785 eV meant that in approximately 50% of the cases a deposition step was performed rather than a KMC step, resulting in a lot of wasted transition searches, but a
long time evolution. It took approximately one week computational time running on 8 processors to provide 1.30 seconds simulated time. A snapshot of the KMC is given to provide an insight into the global behaviour. The growth after 30 KMC steps is shown in Figure 8.20.

The output from the KMC step following this configuration is shown in Table 8.2. The two barriers specified give the NEB calculated barrier along with the coarse estimation of the saddle point found using the RAT method. The probability is calculated using the Arrhenius equation as
KMC Code finds 6 Unique dimer transitions

| Transition 0: NEB Barrier: 1.845, Barrier: 1.948, probability: 2.677e-14, Function Calls: 371 |
| Transition 1: NEB Barrier: 1.286, Barrier: 2.653, probability: 2.95e-06, Function Calls: 296 |
| Transition 2: NEB Barrier: 0.960, Barrier: 0.755, probability: 0.1488, Function Calls: 439 |
| Transition 3: NEB Barrier: 0.693, Barrier: 0.884, probability: 1042, Function Calls: 165 |
| Transition 4: NEB Barrier: 0.604, Barrier: 2.318, probability: 19939, Function Calls: 287 |
| Transition 5: NEB Barrier: 1.780, Barrier: 2.597, probability: 2.331e-13, Function Calls: 386 |

KMC finds: 1 external events
Event: 4, chosen from transition list
Barrier is: 0.604214200001934
Time is: 0.146526883202171

Table 8.2: The output from step 30 of the OTF-KMC.

mentioned previously and the number of function evaluations is given for each search. A benefit of the RAT method that is evident in these results is that the lower energy transitions are generally found in fewer function evaluations then those that are more complex. The roulette wheel chooses transition 4 which is unsurprising given the far greater probability then the other transitions, and the cumulative simulation time is updated at the bottom of the file. In this case there are 6 unique transitions despite the upper limit of 5 as the master process checks the time and search termination criteria at a frequency of once every 10 seconds and on this occasion a 6th unique state was found almost immediately after the 5th. The result of undergoing transition 4 is shown in Figure 8.21 and shows the formation of a more ordered structure on the TiO$_2$ surface.

Figure 8.21: The lattice performing a 0.604 eV transition in the KMC. The atoms are coloured by proximity to the viewer to make the ad-units clearly visible.

The RDF plots of the 300 K MD grown lattice versus the KMC grown lattice shown in Figure 8.22 demonstrate that there is a clear improvement in the structure of the formed rutile when grown
using KMC. So that both lattices were at similar stages of development the MD grown lattice after
115 depositions at 300 K was taken and relaxed before comparison to the KMC results. While the
KMC simulated approximately 1.3 real seconds, the MD simulation has modelled just $1.15 \times 10^{-10}$
s. The hope with KMC is that the transition steps between depositions will allow the possibility of
Ti interstitials annealing, something which is partially borne out when comparing the number of Ti
interstitials in the KMC formed substrate to the 300 K MD grown substrate. The original substrate
from the KMC growth contains just 3 interstitial atoms and all within the 4th layer, while the MD
simulated growth contains 5 interstitials within the substrate, with 1 interstitial atom in the 3rd layer.
This comparison is not entirely fair as the MD growth was performed with a mixture of clusters while
the KMC deposited only TiO$_2$, however when combined with the RDF plots we have good evidence
that the use of KMC allows for more realistic, defect free rutile growth in line with the behaviour
seen when depositing at increased temperatures.

8.7 Conclusions

8.7.1 Rutile

The first conclusion is that modelling growth of rutile allows for some confirmation of the validity
of the MQEq potential. It is one thing for a potential to relax a pre-existing lattice structure and
8.7. CONCLUSIONS

The results from depositing clusters onto a substrate that is heated to just 300 K correlate well with the previous chapters; the large numbers of interstitials formed during deposition supports the single molecule deposition results, while the few Ti interstitials that anneal during growth validate the high Ti interstitial escape barrier evident in the molecular statics chapter. It was hypothesised that the primary mechanism for growth would centre on the mobility of the Ti interstitials combined with the presence of oxygen ad-atoms. Growth simulations verified this and found highly mobile Ti atoms that were able to migrate through successive layers during the growth process. The Ti replacement process is so prevalent that nearly half the interstitials in the upper most layer of the original substrate were replaced by incident Ti atoms via an exchange process during the 300 K growth.

Increasing the temperature to a point such that the scaling of barriers near to 1 eV was similar to the increase in deposition frequency resulted in improved rutile growth. While the scaling in attempt frequency is non-linear, the relative error in attempt frequency for the lowest diffusion barriers is less than the relative increase in deposition frequency, thus the growth behaviour should be closer to the industrial behaviour than growth simulated at 300 K. The single molecule deposition results suggested that the increase in the number of interstitials when moving from 20 eV to 40 eV was far from linear and there would be large numbers of residual interstitials. This was found to be the case, although the relative change in interstitials from 20 eV to 40 eV from growth was not proportional to the relative increase during single molecule deposition simulation.

Having settled on 20 eV due to the lower number of defects it was possible to investigate the influence the stoichiometry would play on the quality of grown crystal, this was equivalent to increasing and decreasing the oxygen partial pressure during the industrial growth process. It was likely that an excess of Ti would result in highly defective growth with large numbers of Ti interstitials, however the formation of sub-surface Ti vacancies in saturated regions had not been previously seen and clearly requires a critical mass of local Ti interstitials. It is likely that eventually a Ti deficit would result in amorphous crystal formation. It was surprising to see that an excess of oxygen results in near perfect growth. Despite the increase in the numbers of oxygen atoms that were incident on the surface, once saturated the oxygen atoms were reflected with a high frequency ensuring that...
the stoichiometry within the grown layers remained perfect. This seems to suggest that if a perfect rutile crystal is desired an increased oxygen pressure will show improved crystal formation during the industrial growth process.

The results from depositing individual atoms versus full TiO$_2$ clusters were easier to predict. When depositing larger clusters far fewer defects were formed and thus were annealed rapidly resulting in perfect growth. One aspect that was not expected when depositing mostly individual atoms was that the crystal would remain structured. As previously mentioned, an excess of Ti resulted in Ti vacancies and general disorder of the lattice resulting in an amorphous like structure within the top few layers, however, when depositing individual Ti atoms the structure remained, with most oxygen atoms occupying valid sites. The increase in Ti atoms below the surface with many valid and interstitial sites occupied, coupled with the under-stoichiometric ratio brings to mind the Magnéli Ti$_n$O$_{2n-1}$ phases.

### 8.7.2 Amorphous and Anatase

It seemed likely that the formation of rutile crystal was largely due to the bias of a rutile substrate which sets the template for growth of future layers. The importance of this template was investigated and simulated growth on an amorphous substrate demonstrated only slight evidence for the formation of a crystal structure judging from the relative RDF plots. However, as with the growth of rutile TiO$_2$, by biasing the deposition such that mostly larger clusters were deposited a slight improvement to crystal structure was evident. Considering some atoms within the substrate are fixed in order to allow deposition it would be very hard for atoms within the simulation to reconstruct to form rutile in the small region of space they occupy. It is likely that further growth modelling, particularly of large cluster based depositions, would result in the formation of a more crystalline structure.

While the amorphous behaviour was similar to that seen when growing on the rutile substrate, the anatase substrate behaved quite differently. It has been shown experimentally that anatase reconstructs at high temperatures [75, 90, 74] and it was interesting to find similar behaviour occurring when simulating the substrate at 1000 K using our empirical potential. Additionally, when depositing large clusters as opposed to a mix of species the anatase appeared to produce poorer crystallinity in the formed layers. By switching to a lower temperature and modelling growth at 300 K with low energy depositions it was possible once again to retain some of the crystallinity of the original substrate,
although the grown layers were poorly ordered. It seems that depositions at 1 eV produced optimum
growth, however, due to the low temperatures involved there was little time for defects to anneal
before subsequent depositions occurred. In order to accurately model anatase growth it is likely that
some means of accelerating the time-scale without increasing temperature is used, such as OTF-KMC.

8.7.3 OTF-KMC

The on-the-fly kinetic Monte Carlo simulation was successful in that it was one of the first times the
long time scale technique has been applied to such a complex system for growth. Formation of rutile
layers at industrial temperatures was successfully simulated and found to produce good crystal when
depositing TiO\(_2\) clusters at 20 eV, as would be expected given the previous work. Through allowing
the KMC long periods to perform steps, many interstitials could escape between depositions, thus the
KMC was able to produce much improved crystal formation when compared to the similar mixed
cluster deposition at 300 K, modelled using classical MD. The total time of 1.3 seconds the simulation
covered far exceeds the time that can possibly be achieved using classical MD.

Unfortunately while the KMC was successful in many respects, some serious approximations
had to be made in order to complete the simulation. If a transition barrier below 0.5 eV is crucial
to the realistic behaviour of the TiO\(_2\) structure during growth then this would have been missed
due to the transition blocking. Additionally by only considering 5 transitions at a time, the time
of the simulation is rendered inaccurate, if not the statistical behaviour. However, despite these
approximations, the behaviour of the lattice during the growth process appears to be realistic, the
crystal structure is much like what would be expected if a real MD simulation was possible over such
a long time-scale and the method shows great promise for future applications.
Chapter 9

Conclusions

The goal of this research project was to model the growth of TiO$_2$ such that some of the mechanisms behind surface growth could be understood. While there are many interesting polymorphs of TiO$_2$ it was necessary to limit the scope of the research primarily to the commonly occurring rutile phase with the (1 1 0) preferential surface, in order to allow a thoroughly analysis of the properties and behaviour of the material within the time-scale of this project. It was clear from the outset that the use of an empirical potential with classical MD would be necessary as the dynamics of growth would be beyond the scope of DFT simulation, however, it was not clear that pre-existing TiO$_2$ potentials would provide the accuracy required to have confidence in the resultant characteristic behaviour.

Two of the most commonly used potentials, the Matsui & Akaogi fixed charge potential and the Hallil et al. variable charge potential were thoroughly investigated with many energetically accessible ad-atom and defect diffusion barriers compared to equivalent DFT behaviour. The fixed charge potential was found to provide excellent agreement with DFT for certain cluster diffusion barriers, such as the TiO$_2$-I to TiO$_2$-I slide along the surface, however, it failed to produce sensible behaviour when dealing with non-stoichiometric systems, such as a single Ti or oxygen ad-atom. The QEq potential was found to improve on the fixed charge potential in many cases with sensible barriers and accurate binding sites for many configurations and even more impressively the accurate recreation of almost all ad-atom configurations on the lattice surface. The DFT results suggested that although a Ti-I interstitial could form with a relatively low barrier of 1.6 eV, the escape barrier was an inaccessible 3.51 eV. The standard QEq produced a similar escape barrier while underestimating the formation barrier to such a degree that Ti interstitial formation using the QEq potential was $8.16 \times 10^9$ more
likely than the equivalent process using DFT when simulating at 350 K.

The inability of Ti interstitials to readily escape according to the DFT was of concern until the influence of neighbouring oxygen atoms was investigated and it was found that with the presence of 2 oxygen ad-atoms the Ti interstitial escape barrier was just 0.559 eV. Had the QEq potential been able to recreate this it may have proved suitable for growth modelling despite the increased frequency of Ti interstitial formation, however, when investigating the Ti escape barrier in the presence of 2 oxygen ad-atoms the original QEq potential produced a barrier of 1.62 eV. The QEq potential indicated that the formation of a Ti interstitial from a TiO$_2$ unit was more likely then the escape of a Ti interstitial on its own, this was completely the reverse of the DFT predicted behaviour. It was clear that growth using the fixed charge potential would bear no resemblance to realistic behaviour due to inaccurate binding sites, stoichiometry issues and the lattice reconstruction when Ti atoms penetrate the surface. Similarly, it seemed likely that growth modelled using the QEq potential would result in massive numbers of Ti interstitials with no realistic escape mechanism at the temperatures being considered.

As the QEq potential produced excellent behaviour for the most part it was used as a basis to develop a new potential that provided better agreement with the DFT results for transitions that were likely to be crucial during the growth process. An investigation into why the QEq produced inaccurate behaviour when modelling the formation of a TiO$_2$ unit from a Ti interstitial and a pair of oxygen ad-atoms revealed that excessive charge transfer was energetically penalising the configuration, with empirical potential charges compared to those produced using Bader analysis of the DFT results. Hallil’s suggested oxygen hardness was lower than the original value given by Rappé and Goddard and it was found that by increasing the oxygen hardness and thereby penalising charge transfer it was possible to bring the escape barrier closer to that found using DFT. The finally selected oxygen hardness of 18.3 eV was 50% greater then the original hardness, however, the escape barrier was reduced significantly to 0.761 eV, much closer to the DFT result and very close to the experimentally predicted value of 0.802 eV. There were some penalties for the change in oxygen hardness, the most obvious being the loss of the TiO-III and TiO-IV binding sites, however it seemed highly likely that both lost binding sites would not play a crucial role during the growth process due to the ease with which they would collapse into the TiO-I and TiO-II configurations respectively.

The DFT results showed that oxygen ad-atoms play a crucial role in the escape of the Ti interstitial, however, this relies on the oxygen atoms being highly mobile, able to migrate along the ad-rows
before binding in the region of an interstitial defect. The oxygen mobility was evident from the
diffusion barriers along the surface for oxygen of 0.286 eV and for O\textsubscript{2} of 0.127 eV, however, the QEq
potential predicted oxygen diffusion barriers of 0.801 eV, thus it was clear that even if interstitials
could escape in the region of oxygen atoms, there would be no mechanism for the oxygen atoms
to rapidly reach the Ti interstitials. Given the very low diffusion barrier of O\textsubscript{2} using DFT, it was
decided that the introduction of an attractive O-O interaction to the QEq potential might allow for
rapid O\textsubscript{2} diffusion using an empirical potential. It was necessary to introduce a potential that allowed
correct O\textsubscript{2} behaviour away from and on the surface of the lattice, but in bulk the standard QEq
Buckingham behaviour would be preserved. To keep things simple a Lennard-Jones interaction was
used to provide the attractive oxygen component, which produced the correct binding energies and
bond-length, combined with an aggressive screening function that would heavily damp the attractive
component as the atom became surrounded by neighbours. This worked extremely well and produced
total screening and purely repulsive interaction almost immediately within the lattice, however, it
was necessary to reduce the O\textsubscript{2} binding energy to below the typical values in order to preserve
sensible ad-atom/surface binding energies. These modifications allowed the creation of two addition
binding configurations that were produced using DFT, the first and most important being the O\textsubscript{2}
ad-molecule in the surface trench and the second being the ad-row O\textsubscript{2} molecule which was deemed
to be unimportant to lattice growth. The modifications resulted in an O\textsubscript{2} diffusion barrier of 0.627
eV which, whilst higher than the DFT predicted result, was lower than any other oxygen diffusion
barrier using the original QEq potential. Thus, through comparison of the empirical potentials to
DFT results via the investigation of many surface binding energies and diffusion barriers, it was
possible to develop a new MQEq potential which would be able to more accurately simulate growth
and allow for perfect crystal formation under the correct deposition conditions, something which was
extremely unlikely with the original QEq.

When modelling growth dynamics it was observed that the surface would form clusters of interacting
ad-atoms with many complex processes occurring. To simplify matters the behaviour of clusters
impinging on the perfect substrate was investigated separately from growth so that the influence
that composition and deposition energy would play on various statistical attributes could be better
understood. It was only necessary to deposit within a small window on the lattice surface due to
the surface symmetry and performing 20,000 depositions of different clusters and energy allowed an
interesting insight into both statistical averages and the destructiveness of deposition as a function of incidence. While it is difficult to see the industrial applicability of the damage as a function of impact site, it is still interesting to see unexpected behaviour such as the inversion of primary damage regions simply by performing oxygen deposition at 20 eV rather than 10 eV. The scope of the information that could be acquired was found to be limited in many cases due to role of cluster orientation; when depositing TiO, O\textsubscript{2} and TiO\textsubscript{2} it seemed that in most cases the damage was randomly distributed, suggesting that the orientation of the cluster was as significant as the contact point.

Some emergent behaviour was obvious for the single atom depositions; the centre of the central surface oxygen atom, the 6-fold co-ordinated Ti atom and the edge of the oxygen ad-row atom were all found to produce high levels of damage for various combinations of cluster and energy. The single molecule deposition validated the behaviour predicted from the ‘Binding Sites and Barriers’ chapter, in particular showing the formation of large numbers of interstitials as the primary and most common defect. New and unpredictable behaviour was seen such as the frequent reflection of oxygen atoms when depositing oxygen atoms and O\textsubscript{2} molecules. More surprising was the drop in the number of reflected atoms as a function of deposition energy; it seems probable that as the cluster energy increases the probability of reflection would also increase, however, when depositing oxygen at 30 and 40 eV the probability of reflection is significantly lower than when depositing at 10 eV. As expected, large numbers of Ti interstitials formed when depositing single Ti atoms, but it was unexpected that the probability of forming no defects would be almost zero with two interstitials forming from a single Ti deposition almost as frequently as one.

At 40 eV it was clear from the results that large numbers of interstitials and vacancies would be formed, with all clusters involving Ti having the potential to form up to 5 interstitials from a single impact. Rather than increasing linearly, the relative change in the number of interstitials drops as we reach 40 eV, this was likely due to the large numbers of interstitials occupying near surface interstitial locations and thus saturating the subsurface region. The idea of interstitial site saturation is further validated through the jump in the average numbers of interstitials penetrating to the 2nd lattice layer at 40eV; when looking at TiO deposition we find that the probability of forming 2nd layer interstitials is more than twice that at 30 eV. In addition to large numbers of defects at 40 eV, it seems likely that with greater than 10% of depositions producing 2nd layer interstitials, growth will be highly defective as it will be difficult for deep interstitials to anneal. Another interesting
property that emerged when performing the single molecule depositions was the relationship between
the numbers of interstitials that were formed directly or indirectly via an exchange; it was surprising
to find an extremely consistent ratio of 30% of all interstitials being formed directly at almost all
energies for all clusters involving Ti.

Most of the behaviour observed during the investigation into single molecule deposition was
predictable. For example, the numbers of vacancies and interstitials generally increased as a function
of energy. It became possible to draw the conclusion that growth at 40 eV would produce severely
inhibited and possibly amorphous growth due to deeply embedded and relatively immobile interstitials,
while growth depositing TiO$_2$ units with lower energies such as 20 eV would produce far fewer
interstitials and thus more crystalline growth, something confirmed in the following chapter.

The analysis of the 10 most frequently occurring ‘defects’ was interesting. It was unsurprising
that the top defect consisted of a single oxygen ad-atom as a vast number of single oxygen depositions
resulted in just that, whilst the Ti-i-I interstitial being the second most common defect was also
predictable. It was interesting that the top 10 most common defects included a complex configuration
that involved 3 vacancies, 2 interstitials and an ad-atom, something that occurred during 244 deposition
simulations and was more frequent then many of the simple binding configurations investigated in
the ‘Binding Sites and Barriers’ chapter. The means of identifying and classifying the defects was
an interesting and useful exercise. Through applying graph theory to molecular clusters it became
possible to classify and group identical defects regardless of symmetry or orientation, something that
has potential applications far beyond those utilised in this research.

The modifications to the QEq potential were somewhat validated when the growth of rutile was
successively simulated with sensible behaviour at industrial temperatures and deposition energies.
It was necessary to increase the flux rate of TiO$_2$ clusters onto the lattice in order to achieve
sensible computational time-scales when simulating growth. Previous results had indicated that large
numbers of interstitials would form and that the interstitials would not have enough time to anneal
between successive depositions, so it was not surprising that the growth at 300 K was highly defective
with large numbers of residual interstitials. The suggested mechanisms for growth, involving direct
interstitial formation via incident atoms followed by an exchange mechanism to push the Ti atom out
of the surface, was proven to be valid through tracking the evolution of various Ti atoms during the
simulation. Many Ti atoms were found to follow a cycle between interstitial and lattice sites as they
climbed the lattice. Further support was seen in the large numbers of Ti atoms that were replaced in the surface of the original substrate.

Through heating the lattice to 1000 K it was possible to scale the attempt frequency of a transition with a barrier of 1 eV to a similar degree to the increase in flux, thus allowing diffusion of oxygen ad-atoms and Ti interstitials within the deposition timeframe. This was successfully applied to model growth at 20 eV and found to significantly reduce the numbers of residual Ti interstitials as was hoped. Despite the acceleration of dynamics it seemed likely that depositing a mix of clusters at 40 eV would still produce defective growth, predominantly due to the increased formation of 2nd layer interstitials which annealed slowly and this was also found to be the case with the radial density plots demonstrating that growth at 20 eV provided a superior correlation with the perfect substrate.

Having satisfied that increasing temperature compensated for the accelerated TiO$_2$ flux, the influence of cluster composition was investigated. It was unsurprising that depositing a non-stoichiometric mix with a preference for Ti produced severely defective growth, with the potential for eventual amorphous growth. However, it was unexpected that the oxygen excess resulted in perfectly stoichiometric crystal growth in a self limiting process. The results of the cluster size were less surprising; depositing predominantly single atoms allowed large numbers of interstitials to form and frequent oxygen reflection resulted in poor stoichiometry and crystallinity. Depositing full clusters produced perfect growth at 20 eV, something that seemed likely given the behaviour seen in the ‘Single Molecule Deposition’ chapter and led to the conclusion that an increase in oxygen pressure during the industrial process would produce better rutile growth, partly through oxidisation of the TiO$_2$ surface and partly due to additional oxidisation of Ti plasma on the way to the substrate.

Depositing TiO$_2$ onto an amorphous substrate initially provided disappointing results as the growth seemed to remain amorphous with little evidence of crystallinity. However, when depositing predominantly larger clusters there was some evidence for more structured growth formation when comparing both growth RDF plots to the perfect rutile substrate. It is quite possible that the amorphous growth is primarily due to constraints of the system such as the limited number of depositions and the fixed atoms at the bottom of the amorphous substrate, allowing little room for reconstruction.

The initial investigation into anatase growth was similarly disappointing with a simple heating of the substrate to 1000 K resulting in reconstruction and further depositions of a standard cluster mix
along with depositions of predominantly larger clusters producing highly amorphous growth with little in common with the anatase substrate. However it has been shown that anatase reconstructs to form rutile at high temperatures and it was possible that the decay into amorphous TiO$_2$ was due to the energetic unfavourability of anatase at higher temperatures rather than an artefact of the potential. Repeating the growth simulations at 300 K supported the idea that the anatase structure was unstable only at higher energies with improved crystal structure if not perfect anatase growth. One respect in which anatase differed from amorphous and rutile growth was that the deposition of larger clusters resulted in more defective growth then the original mix of probabilities. The conclusion is that it is infeasible to investigate growth mechanisms for anatase with the lattice heated to 300 K as there is little time for defects to anneal before successive depositions.

Having demonstrated that growth is dependent on the formation and subsequent annihilation of Ti interstitials it seems odd that the rutile (1 1 0) surface can also be formed via evaporation and chemical solution methods. When considering these alternate formation processes it is necessary to note that a stable TiO$_2$ unit relaxed on the (1 1 0) surface will eventually result in a Ti-i-II interstitial once successive oxygen atoms have been deposited. As such we would expect to see the same low energy Ti annihilation processes providing a critical role using other TiO$_2$ growth methods.

The most ambitious part of this research project was the attempt to simulate growth over long time scales at industrial temperatures using the on-the-fly kinetic Monte Carlo method. The initial challenge was the implementation of an efficient transition finding algorithm, which proved to be far harder than expected. The dimer method had previously been applied with much success to more simple dynamical KMC problems and found to provide reasonable performance and so it was implemented early in this research project with an improved rotational minimisation algorithm. While the dimer method provided excellent performance when tested with simple problems such as the diffusion of vacancies and ad-atoms on silver, it proved inefficient when dealing with larger clusters on the TiO$_2$ surface with many function evaluations required for convergence on each saddle point. Next the activation and relaxation technique was implemented. This is simpler than the dimer method and often finds lower energy barriers more rapidly. However, when using the ART, certain saddle points proved difficult to locate due to the monotonic constraint inherent in the method. Finally a simple algorithm was developed which borrowed ideas from both the dimer and ART and succeeded in finding a fuller set of saddle points surrounding a minimum while converging on lower energy saddles.
more rapidly than the dimer method. All three methods were used to try to ensure that the full set of low energy transitions for simple ad-clusters and defects was explored in the ‘Binding Sites and Barriers’ chapter.

Despite the improvements in performance due to the use of the RAT method it was clear that the KMC would not provide satisfactory performance unless it was efficiently implemented. It was necessary to parallelise the operation of the KMC such that the transition searches, the relaxation into adjacent minima and the use of the NEB to find the true barrier, were all executed on separate processors. While the bulk of the simulations were performed on an 8-core machine, it was necessary to support SSH execution of jobs on external computers such that up to 32 transition searches could be performed simultaneously. Once completed the KMC program was able to perform rapid transition searches and could evolve complex defects through steps far more rapidly than achievable with classical MD. The method was also utilised to simulate defect diffusion after cascades in plutonium [83]. While successful in modelling the early stages of TiO$_2$ growth, the KMC rapidly became dominated by low energy barriers that were not conducive to crystal formation yet occurred with a high frequency. In addition, the implementation of Mousseau’s ‘tabu’ transition blocking algorithm succeeded only in extending the simulation time before low energy barriers dominated the KMC simulation offsetting the time benefit over MD.

In the end it was necessary to make some approximations in order to ensure rapid evolution of the KMC such that multilayer growth could be simulated. Through restricting the considered transitions to those greater than 0.5 eV the time-scale was instantly accelerated at the cost of missing all transitions below 0.5 eV, including any that might play an important role in growth mechanics. Similarly by reducing the number of unique transitions to just 5 at each time step the full range of escape routes for each configuration were not sampled, therefore important transitions might have been missed and the time evolution was less accurate. Despite this, there can be some confidence that the growth behaviour is similar to realistic dynamics due to the tendency of the RAT method to converge on lower energy saddle points with fewer function evaluations. Thus the KMC simulation was likely to find the lowest barrier transitions for any given configuration. Additionally, any low energy transitions that were crucial to growth could freely occur during the MD depositions.

The emergent growth dynamics in the approximated KMC closely resembled those seen when performing high temperature MD growth and a video showing the evolution of the lattice at each
KMC step closely resembled videos of classical MD. Further, the KMC produced very similar results to those seen when modelling growth, with fewer numbers of defects than the MD growth at 300 K, due to the KMC steps annealing the Ti interstitials. The KMC grown lattice did contain residual interstitials, unlike the large cluster based growth at 1000 K, however, this is readily explained by the vast increase in attempt frequency for Ti interstitial escape at 1000 K, exceeding the increase in TiO$_2$ flux. As such it seems the KMC has been highly successful in allowing simulation of growth over a time-scale of 1.3 s, far beyond the reach of classical MD and demonstrating the potential of this technique for future applications.

This research project has provided an excellent insight into the growth dynamics of TiO$_2$ deposited onto the rutile (1 1 0) surface at industrial temperatures and energies. Growth on anatase and amorphous has been investigated and understood to a lesser extent, but insight into the optimum growth parameters for both forms of TiO$_2$ has been provided. Realistic behaviour over long time-scales has been achieved through temperature based diffusion acceleration and using the more cutting edge OTF-KMC long time-scale technique. Most importantly, a good understanding of the critical processes vital to rutile crystal formation has been acquired along with conclusions regarding the optimum conditions to produce crystal growth in the industrial environment.

9.1 Future Work

While a good understanding of the (1 1 0) preferential surface of the rutile polymorph of TiO$_2$ has been achieved, the (1 0 0) surface which is also stable has not been investigated. Further research might investigate the binding sites and transition barriers for clusters on other energetically stable surfaces of rutile in addition to anatase. The influence of depositions on the most stable (1 0 0) anatase surface should be investigated as it seems the results would differ strongly to those seen with rutile, with a high possibility of lattice reconstruction in the impacted region. Growth on the amorphous surface should be simulated for longer time-scales, with greater numbers of depositions onto a larger substrate in order that reconstruction could more readily occur. Further growth would also allow the influence of larger clusters on the crystallinity to be investigated such that the marginal improvement seen in this research project could be confirmed.

The KMC simulation currently provides interesting results, however, it is biased and it is difficult to be confident that accurate behaviour is being witnessed. Some means with which to allow rapid
evolution to occur needs to be investigated. Henkelman has suggested [102] a means by which low energy barriers are systematically explored along with their escape saddles until a super-basin can be constructed containing only those barriers that are large enough to be of interest. This avoids the high frequency vibration between the low energy sites while providing accurate probabilistic behaviour. This exploration process will be computationally expensive, however, it will allow the system to evolve far more rapidly then would naturally occur during the KMC simulation.

The concept of an isomorphic graph to describe defect configurations was introduced in this thesis, however, it was of limited application. In the future, rapid invariant defect categorisation could prove extremely useful. Consider the evolution of defects within a closed system such a number of interstitials in the bulk of the lattice. Currently the KMC would constantly perform fresh transition searches for each new configuration in 3N dimensional space, where N is the total number of atoms. In practice it is necessary only to perform fresh transition searches when the configuration of the interstitials relative to each other changes, i.e. 2 adjacent interstitials perform the same transitions regardless of their absolute position within the bulk. Through the isomorphic signature it becomes possible to invariantly save the configuration of each defect such that at each KMC step, rather than comparing absolute lattice configurations we need to only consider each defect configuration. If a new configuration is found to be isomorphically equivalent to a previously searched configuration the previous transition can automatically be mapped onto the current configuration without performing further transition searches. This would allow all the advantages of OTF-KMC with realistic diffusion behaviour and the potential for novel and unpredictable transitions while providing the same performance as a standard rigid KMC model.

While the OTF-KMC was applied to model rutile (110) growth, it seems that the anatase (100) surface presents the ideal candidate for future work involving the OTF-KMC technique. This is due to the fact that accelerating dynamics thermally, produces lattice reconstruction and hence provides meaningless results. If the KMC can be improved such that realistic results can be acquired without making some of the compromises seen in this research project, it could potentially model anatase growth, something seemingly impossible with standard MD.
Bibliography


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