Dynamical simulation of multicomponent carbon based materials

This item was submitted to Loughborough University’s Institutional Repository by the/an author.

Additional Information:

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

Metadata Record: https://dspace.lboro.ac.uk/2134/13151

Publisher: © Keith Michael Beardmore

Please cite the published version.
This item was submitted to Loughborough University as a PhD thesis by the author and is made available in the Institutional Repository (https://dspace.lboro.ac.uk/) under the following Creative Commons Licence conditions.

For the full text of this licence, please go to: http://creativecommons.org/licenses/by-nc-nd/2.5/
Dynamical Simulation of Multicomponent Carbon Based Materials

by

Keith Beardmore

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology.


© by Keith Michael Beardmore, 1995
Abstract

This thesis describes the simulation of important dynamical processes involving carbon based materials. Much of the research has been aimed at examining the properties of C60 (buckminsterfullerene), the recently discovered third allotrope of carbon. Classical Molecular Dynamics (MD) simulation has been applied to study such diverse processes as fullerene film growth, the interaction of fullerenes with graphite and bare and hydrogen terminated crystal surfaces, and the implantation of atoms within C60. We have also studied radiation damage to polymers and graphite. Collaboration with experimentalists has resulted in realistic simulations being conducted to examine physical processes. The results of simulations have been able to explain experimental results and suggest alternative methods of achieving the goals of the experiment.

Several algorithms designed to improve the efficiency of simulations have been programmed and tested. Timing results for these various algorithms are presented and the most successful have been incorporated into a new MD simulation code. This has enabled systems of up to 100,000 atoms to be studied in a realistic time using single workstations (e.g. IBM RS6000 and SUN Sparc-10). The interaction of atoms is modelled by many-body potential functions. Several potential functions that describe covalent systems have been programmed. New potential functions have been produced to model the long-range interactions that occur in graphite, fullerite and polymer systems, and a three-component, many-body potential has been developed for the accurate and efficient simulation of carbon-silicon-hydrogen systems. Computer visualisation and animation techniques have been applied to the interpretation and display of simulation results.
Acknowledgements

It is a pleasure to thank my supervisor, Roger Smith for introducing me to this field of research, and whose enthusiasm and guidance have been invaluable throughout my study. Thanks must also go to Roger Webb, Ivan Chakarov and Asta Richter for their helpful advice and many useful and interesting discussions. I should also like to express my gratitude to Keith Watling, who spent many hours installing public domain software to enable computer visualisation and animation to be used. I must also take this opportunity to thank my family and friends, for their encouragement and support throughout my studies. Finally, I would like to acknowledge the EPSRC for the funding that has enabled me to carry out this research.
The Autoverse was ... a computer model which obeyed its own simplified 'laws of physics' - laws far easier to deal with mathematically than the equations of real-world quantum mechanics. Atoms could exist in this stylised universe, but they were subtly different from their real-world counterparts.

Greg Egan, *Permutation City*
Contents

1 Introduction
  1.1 Overview ....................................................... 8
  1.2 Layout of Thesis .............................................. 16

2 Molecular Dynamics Algorithms
  2.1 Introduction .................................................. 17
  2.2 The Basic Classical MD Algorithm .............................. 18
    2.2.1 Introduction .............................................. 18
    2.2.2 The Computational Box .................................. 19
    2.2.3 Boundary Conditions ................................... 20
    2.2.4 Potential and Force Calculations ......................... 21
    2.2.5 Integration ............................................... 22
  2.3 Efficient Evaluation of Forces .................................. 22
    2.3.1 Introduction .............................................. 22
    2.3.2 Evaluation of Potential Functions ......................... 23
    2.3.3 Neighbour-Lists Methods .................................. 24
    2.3.4 Infrequent Neighbour-List Update ......................... 29
    2.3.5 Data Structure ............................................. 30
    2.3.6 Many-Body Potentials .................................... 34
  2.4 Integration of Trajectories .................................... 35
    2.4.1 Integration Schemes ...................................... 35
    2.4.2 Variable Timesteps ....................................... 37
  2.5 Finite Temperature Simulations ................................ 40
    2.5.1 Adding Temperature to the System ......................... 40
    2.5.2 Temperature Control ....................................... 40
  2.6 Selection of Representative Trajectories ....................... 42
  2.7 Analysis of Simulation Results .................................. 43
  2.8 Visualisation and Animation .................................... 46
  2.9 A New Molecular Dynamics Program .............................. 49
4 Energetic C\textit{60} Interactions with Silicon Surfaces
4.1 Introduction .................................. 119
4.2 Comparison of Interactions with Bare Silicon Surfaces .... 120
4.3 Investigation of Hydrogen Terminated Surfaces .......... 133
4.4 Conclusions .................................. 142

5 Fullerene Film Growth on Silicon
5.1 Introduction .................................. 144
5.2 Simulation of Film Growth on Si\{100\}(2\times1) .......... 146
5.3 Conclusions .................................. 151

6 Ion Bombardment of Graphite
6.1 Introduction .................................. 152
6.2 Simulations Using Tersoff's Potential .................. 154
6.3 Simulations Using Heggie's Potential .................. 156
6.4 The Displacement Threshold Energy for Graphite .... 159
6.5 Conclusions .................................. 165

7 Ion Bombardment of Polyethylene
7.1 Introduction .................................. 166
7.2 Details of the Calculation ........................ 167
7.3 Single Impact Simulations ........................ 170
7.4 Multiple Impact Simulations ........................ 175
7.5 Conclusions .................................. 175

8 The Interaction of Hydrogen with C\textit{60}
8.1 Introduction .................................. 177
8.2 Experimental Details ........................... 178
8.3 Preliminary Calculations ........................ 180
8.4 Interactions with a 'cold' C\textit{60} Lattice .......... 187
8.5 Interactions with 'heated' C\textit{60} .................. 194
8.6 Conclusions .................................. 199

9 Summary, Conclusions and future work
9.1 Summary and Conclusions ........................ 201
9.2 Future Work .................................. 204

References ...................................... 208
Chapter 1

Introduction

1.1 Overview

The last 40 years has seen the development of a new approach to the investigation of chemical and physical phenomena. Traditionally, this investigation has been divided between experimental and theoretical approaches. The advent of scientific computing in the 1950s enabled previously intractable problems to be examined via computer simulation, and simulation techniques have evolved in parallel with computer technology. Today, computer simulation is used in the investigation of phenomena, ranging from the interaction of quarks within a proton or neutron studied by quantum chromodynamics (QCD), to the collisions of galaxies moving under gravitational attraction, and is used in many more areas outside the physical sciences.

This thesis is concerned with the simulation of materials on the atomic scale. The molecular dynamics (MD) simulation method is used to follow the evolution of a system of discrete particles through time. The physical laws that govern the interaction of atoms are modelled and the behaviour of the complete system emerges as the simulation evolves. Harrison [1] offered the following working definition: a simulation is a model of a physical system expressed as a computer program which enables one to study some aspect of nature by performing numerical experiments upon a mathematical model of a simplified universe. Although the definition is slightly simplistic, it does at least begin to clarify the place occupied in scientific research by simulations. The term 'computer experiment' has often been applied to MD simulations, as the methodology of simulation does have many analogies with experiment. However, simulation is neither theory or experiment, but lies somewhere between the two.

The scale (dimensions, time, energy and complexity) of simulations that may be conducted is to a large extent dependent upon the available computing power. Hence, the field is growing at a rapid rate as computational resources increase and simulators develop ever more complex problems that can be examined by MD.

The first MD simulations were performed by Alder and Wainwright [2] in the late 1950s. They observed phase transitions whilst calculating the motion of a
system of 32 hard spheres within a cube. In later simulations [3], they were able to calculate the equation of state and the collision rate for systems of up to 500 atoms in a cubic cell with periodic boundary conditions applied to the sides.

In the early 1960s, Vineyard et al. conducted simulations of radiation damage in a model representing copper [4]. The model used to represent interactions between atoms was a Born-Mayer function. As this function is purely repulsive, a constant force directed inwards, was applied to all surface atoms to stabilise the crystal lattice. In their calculations, up to around 1000 atoms were simulated, and they were able to calculate the directional dependence of the displacement threshold energy. Collision-replacement sequences were observed along crystal axes, and the configurations of vacancies and interstitials were determined. They later extended their simulations to consider α iron [5], which has a bcc structure, as opposed to the fcc structure of Cu.

Verlet [6] considered the interaction of 864 particles acting through a truncated Lennard-Jones potential in the late 1960s. He also introduced a bookkeeping method that increased the efficiency of his algorithms by a factor of 10. His thermodynamic study of a fluid of atoms showed a striking agreement with the thermodynamics of real argon.

At around the same time, Harrison [1,7] applied the MD simulation method to the study of the ion bombardment of metal surfaces. He was able to investigate the processes of sputtering and crater formation due to ion bombardment of Cu, Rh, Mo, Au, W and other metals. He examined ejection mechanisms, and calculated the dependence of sputtering yield on the energy and angle of incidence of the ion.

The binary collision (BC) approximation was developed by Robinson [8] in the 1970s, to examine radiation effects in crystalline materials. Using this method to study the ion bombardment of silicon, Robinson discovered the phenomena of channelling. Biersack [9] later adapted the method to amorphous materials by calculating the mean free path between collisions. In the BC approach, it is assumed that particles interact pairwise at a time and that the particle trajectories can be approximated by their asymptotes before and after collision and that collisions between moving atoms can be ignored. Hence, particle trajectories are calculated without determining the intermediate dynamics. The approximations used within the BC method mean that a number of processes can be studied that would be too computationally demanding to study by MD. Due to the nature of the assumptions used in the method, it is limited in its applicability. The BC approach is especially suited to the analysis of high energy ion implantation distributions and high energy ion scattering from surfaces. It is unsuitable for lower energy situations, where the paths of atoms cannot be
assumed to be straight lines, multiple collisions are important, or chemical bonding has a large influence on the dynamics.

During the 1980s, many-body potential functions were developed for metals and covalent materials. These types of potentials provide a much more realistic description of materials than pair-potentials. Two of the most successful of these potentials are the embedded atom method (EAM) for metals developed by Daw and Baskes [10,11] and Finnis and Sinclair [12], and the Tersoff-Abell formalism [13] for covalent systems. In the EAM method, each atom is treated as if it is an impurity embedded in a host lattice consisting of all other atoms. EAM potentials have been used by many groups, for instance Bacon et al. have conducted an extensive study of defect production in various metals [14]. As covalent materials involve open structures, in comparison with the close packed structures of metals, they cannot be modelled using pair potentials. The Tersoff potential involves a term dependent upon bond angles that stabilises the structure of covalent materials and models the strain due to bond bending. Tersoff-type potential functions have been used to conduct realistic simulations of many processes occurring within covalent materials. For example, Smith et al. have studied the bombardment of graphite and silicon surfaces by ions and molecules [15-19]. Other MD simulations have investigated the collision of \( C_{60} \) with hydrogen terminated diamond \{111\} surfaces [20]. Taylor and Garrison have used both EAM and Tersoff potentials to study the bombardment of hydrocarbons absorbed on metal surfaces [21].

A new application of MD using many-body potentials is in the developing science of nanotechnology. Molecular gears, constructed from a six-pointed fullerene joined to a nano-tube which acts as an axle, have been proposed [22]. Simulations showed that the gears were capable of being driven at speeds of up to 0.5 revolutions/ps (1/2 trillion revolutions per second), and could be accelerated to these speeds in 10 ps.

The development of efficient ab-initio methods to solve approximations to the Schrödinger equation has further increased the accuracy of dynamic simulations. In 1985, Car and Parrinello used a combination of density functional (DF) theory and MD to simulate a periodically repeated cell containing eight \( Si \) atoms in the diamond structure [23]. They were able to calculate static and dynamic properties of crystalline silicon. Since then, by using supercomputers, the method has been applied to systems of hundreds of atoms. One of the largest simulations carried out to date concerned a ~700 atom model of the \( Si\{111\}(7\times7) \) reconstruction [24]. The calculation was carried out on a Thinking Machine CM-2 with 16,000 processors and 1 gigabyte of memory. The optimised \( 7\times7 \) structure
and the energy difference between the 7x7 and 2x1 reconstructions was calculated.

Recently, a formulation of the tight binding method (TBM) that scales linearly with the number of atoms within the system has been developed [25]. The bond order potential (BOP) includes a degree of quantum mechanical behaviour, but is far faster than full ab-initio calculations. Using BOP, dynamical simulations of systems containing several hundred atoms can be conducted using a computer workstation.

There now exist a whole range of modelling methods, from the binary collision approximation, through pair potentials, three-body and many-body potentials, tight binding approximations, to Car-Parinello and other types of ab-initio calculation. Each type of method has its own advantages and disadvantages, with one of the main criteria for choosing a particular method being a compromise between speed and accuracy of the calculation. As computational resources continue to increase, the use of ab-initio methods will be applied in the study of larger and larger systems. Increased computational resources are not just used to study small systems in intricate detail. Simulations using the same pairwise interaction functions as Verlet's 864 particle simulation of 1967 are still carried out, but on a much larger scale. A simulation conducted using a massively parallel machine in 1994 contained approximately $6 \times 10^6$ particles [26]; an increase of a factor of $7 \times 10^5$ in 27 years.

Visualisation and animation techniques began to be used very soon after the introduction of the MD method; an early development was described by Vineyard et al. [4]: *The positions of selected atoms can be displayed on a cathode-ray screen. Displays are presented sequentially and multi-flash pictures can be taken on stationary film; by advancing the film after each display, moving pictures have been made.* Scientific visualisation techniques are particularly suited for use with the results of simulation, as large amounts of numerical data are readily available for analysis. Visualisation techniques can be used to extract real and meaningful information from the vast amount of data produced by simulation. The vast increase in computational power, the introduction of high-resolution colour monitors, and the free availability of software for the production, transformation, and display of computer images, have made visualisation and animation processes far simpler and much more useful than those first used in the 1960s. Visualisation techniques are used throughout all stages of simulation work. When commencing a new investigation, visualisation of preliminary simulations can be used to indicate processes of interest, which can then be examined by statistically methods. Visualisation and animation are also used when analysing results of simulations, to examine the processes that lead to
the observed data. Finally, visualisation is extremely useful for communicating results of simulations, either as stills or movies, as part of a paper or presentation. The best way to present many results is by animation of typical trajectories, with the movie shown either as part of a presentation, included with a journal paper, or as a component of a hypertext world-wide-web document.

The work contained in this thesis was conducted with two aims. The first was to examine the usefulness and accuracy of computer modelling of dynamical processes using the MD method. At the same time, the simulations that were conducted were required to be realistic and to ultimately produce useful results. Carbon was an ideal material on which to base these studies, as concentrating the research on carbon based materials allowed many different phenomena to be examined. Carbon is particularly interesting as it exists in pure form as three stable allotropes at room temperature and pressure, i.e. the diamond, graphite, and fullerene structures. Carbon is also a component of many other materials that can be simulated, e.g. silicon carbide, hydrocarbon molecules, and polymers. The exceptional physical and electrical properties of this element mean that it has many current uses, and there are many more uses that are proposed. Thus there is a considerable amount of experimental and theoretical data available about this element and its compounds, but there are also areas where data is required and can be obtained by MD methods.

In this thesis, systems of up to tens of thousands of atoms have been simulated for times between one ps and several hundred ps, with energies up to thousands of eV. The simulations were conducted on computer workstations, such as the Sun Sparc-10. For simulations of this size, and with current computer resources, there is no possibility of including any electronic degrees of freedom within the model. Classical MD simulations are used, with most interactions described using various empirical many-body potential functions.

A large amount of the simulation results presented in this thesis are concerned with the interaction of fullerenes with crystal surfaces. Fullerenes are the recently discovered third allotrope of carbon, and were first noticed in November 1985 by Kroto et al. [27]. When graphite was vaporised into a helium gas using a pulsed laser, they recorded the formation of carbon clusters containing up to 190 atoms. Only even numbers of atoms were observed for clusters containing greater than 40 atoms, and under certain conditions, 50% of the total cluster abundance was accounted for by 60 atom clusters. This sixty atom molecule, termed buckminsterfullerene, has the structure of a truncated icosahedron; giving a polyhedron with 60 vertices, 12 pentagonal and 20 hexagonal faces. The \( \text{C}_{60} \) molecules were given their somewhat fanciful name
after Buckminster Fuller who had previously recognised the high stability of similar structures in the design and construction of his geodesic domes [28].

Experiments and simulations impacting $C_{60}$ molecules on various targets [29-33,17,20] have indicated they are extremely resilient. A solid form of $C_{60}$, termed fullerite has been produced at room temperature [34]. This has the face centred cubic structure of many crystals, where fullerene molecules replace individual atoms. Since the discovery of $C_{60}$, a whole new family of related fullerenes have been discovered, including $C_{70}, C_{84}$ and considerably larger molecules [35,36]. Multilayered structures termed 'bucky onions' and single and multilayered nano-tubes with a graphite-like structure [37,38] have also been routinely produced. Multicomponent fullerenes have been suggested following successful substitution of boron into $C_{60}$ to produce molecules such as $C_{(60-n)}B_n\, n=0\ldots6$ [39]. In particular the $C_{12}B_{24}N_{24}$ fullerene is expected to be stable, this molecule contains the maximum number of $B$ and $N$ atoms whilst avoiding any $B-B$ or $N-N$ bonds [40].

There is an increasing interest in the use of clusters as tools for modifying the properties of solids [41]. The evolution of methods utilising clusters is still at an early stage, and is driven by the expectation that cluster impingement on solids will exhibit new effects not present in collisions of individual atoms with those solids. Cluster collisions differ from single ion collisions in several ways. As the kinetic energy of the cluster is divided between tens or hundreds of atoms, individual atoms only posses a fraction of the energy of the total cluster. Hence, even at cluster energies of up to hundreds of keV, the energy goes directly into atomic motion, without the delay that occurs for ions with the same energy, where energy is first converted into electronic excitation. The depth of penetration by clusters is very shallow compared to ions with the same velocity as the large number of simultaneously occurring many-body interactions prevents channelling type motion from occurring. As a cluster approaches a solid, its atoms interact with the surface at different times, so the atoms that collide first with the surface are then impacted by the remaining atoms within the cluster that are still arriving at the surface. This causes the cluster atoms to obtain large lateral velocities, even when the cluster was at normal incidence.

Expected uses for cluster bombardment range from surface cleaning, surface smoothing to sputtering, implantation and film deposition. The use of clusters in ion beam lithography may enable greater precision. A problem with ion beam lithography is that the charges on the ions cause mutual repulsion and hence prevent focusing of the ion beam beyond a certain limit. By utilising clusters, it should be possible to increase the mass : charge ratio by orders of magnitude and hence achieve a thinner beam at the same fluence.
The growth of an amorphous diamond film by low energy deposition of small carbon \((C_{10}-C_{32})\) clusters has been achieved by experiment \([42]\). Raman spectrum analysis indicated the existence of very small \(sp^3\) hybridised clusters in the film. This led to the hypothesis that small fullerenes were produced in the non-equilibrium conditions of the laser vaporisation source. Although clusters of this size prefer polycyclic structures, they are expected to be stable as fullerenes for the time taken for the flight from the source to the substrate. The curvature of small fullerenes causes their atoms to be almost \(sp^3\) hybridised, so they are stabilised by the formation of a fourth bond on each atom by crosslinking on the surface.

Low energy deposition of fullerenes onto a substrate can result in the growth of ordered fullerite films. There is great interest in the formation of these films \([43-52]\), and large amount of experimental work has been concentrated on thin fullerene films grown on silicon surfaces. As the electrical properties of fullerite change from insulator to semiconductor, conductor and finally superconductor depending upon the type of doping, there are many possible applications of a fullerite-semiconductor interface. We have conducted simulations of the initial stages of growth of pure fullerite films on silicon. This has enabled us to observe the growth mode and the dependence of crystal growth on temperature.

We have also conducted simulations of the ion bombardment of graphite. The recent advance in microscopies such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), that are capable of atomic resolution, has enabled the consequences of individual ion impacts on solid surfaces to be studied. The behaviour of graphite surfaces under ion bombardment differs from that of most other materials \([53]\). Similar features are produced on the surfaces of many materials by keV ion impacts, and consist of a crater surrounded by an annular ridge of adatoms, whereas bumps are formed on the graphite surface. MD simulation was used to examine the processes responsible for this behaviour, and to investigate the energy threshold for radiation damage to the graphite lattice.

The bombardment of molecular solids such as polymers with high energy \((500\) eV to \(2500\) eV) particles is an effective method of placing these molecules, as both ions and neutrals, into the gas phase for subsequent analysis via mass spectrometry (MS) techniques, such as secondary ion MS (SIMS) \([21]\). In addition to a peak corresponding to that of the parent molecule, peaks corresponding to fragments of the molecule, and various aggregates of the molecule and fragments are found in the mass spectrum. A number of mechanisms have been proposed for the formation of these detected species, including reactions within the target, at the solid-gas interface, or during the flight.
of ejected molecules to the detector. The processes occurring during the ion bombardment of polymers are also relevant to the use of polymer photo-resists during manufacture of semiconductor devices. The development of multicomponent, many-body potential functions means that realistic simulations can be conducted of these processes. Both qualitative information about the general behaviour of polymers during ion bombardment and quantitative information, such as the mass spectrum of ejected molecules has been produced.

Other simulations that we have conducted have been concerned with the possibility of implanting hydrogen atoms within a fullerene. The stability and size of the $C_{60}$ molecule means that it is possible to produce new materials by implantation of atoms into the cage. A short time after the discovery of the $C_{60}$ molecule, evidence was obtained that a single lanthanum atom could be trapped inside the cage [54,55], and the trapping of other species such as potassium has also been reported. Evidence has also been obtained of the trapping of helium during $C_{60}$ collision with helium gas [35]. The success with metal and helium atoms suggests that it might be possible to implant other species such as hydrogen within the fullerene cage, but experimental attempts to produce the endohedral complex $H@C_{60}$ have so far only resulted in exohedrally bound hydrogen. There are a number of possible applications for $H$ trapped within the $C_{60}$ structure, as endohedral complexes would provide a unique possibility to tailor specific properties of $C_{60}$ systems on a molecular level.

To produce realistic simulations of the systems outlined above, requires simulation times and system sizes that are near the maximum that can be attempted using workstation sized computers. Therefore, it is necessary for the MD program to run efficiently on these types of computers. A new MD code has been developed, specifically to conduct classical simulations, using many-body potentials on workstation computers.

The simulations offer a real test of the available empirical potential functions. The open covalent structure of carbon compounds and the existence of allotropes with very different structures means that sophisticated potential functions are required. In some cases, these simulations have required the production of new potentials, or the modification of existing potentials to ensure that the simulation is accurate. The importance of long-range, non-bonded interactions between atoms has been examined and this has lead to suggestions for incorporating such potentials into simulations involving many-body potential functions.
1.2 Layout of Thesis

This thesis is organised as follows. Before presenting results of the simulations that have been conducted, the computational methods and interatomic potentials used are described.

Chapter two contains a description of the classical molecular dynamics method and its implementation on workstation sized computers. Algorithms for increasing the efficiency of simulations have been examined and this has led to the production of a new, highly optimised MD program. New algorithms have also been developed and these are presented, along with timing results of the program. Methods are also described for using freely available public domain software to efficiently produce high quality movies to illustrate simulation results.

The various potential functions used are detailed in chapter three. A new C/Si/H potential produced by a hybrid of Tersoff-type C/Si, C/H and Si/H potentials is described. This new potential is shown to give a good description of bulk Si and C crystals and small C-Si-H molecules. The necessary steps taken to ensure the applicability of empirical potentials for describing situations not accounted for in their development are discussed. The results of testing and modification of the potential functions to ensure accurate simulations of C60 are described. The development of long-range potential functions for use in conjunction with short-ranged many-body potentials is also detailed.

Chapters four to eight contain details of the simulations conducted to investigate the behaviour of carbon based materials. The majority of this research concerns the interactions of C60 fullerenes in the sub-eV to 5 keV energy range. Chapter four describes the investigation of 50 eV to 5 keV fullerene interaction with bare and hydrogen terminated silicon surfaces. The investigation of the growth of fullerite films on a silicon substrate by low energy deposition is described in chapter five. Chapter six is concerned with the behaviour of graphite surfaces under ion bombardment. The displacement threshold energy for graphite is calculated and the processes responsible for the formation of bumps on the graphite surface are investigated. The results of simulations to study the ion bombardment of polyethylene are presented in chapter seven. Chapter eight is concerned with attempts to produce endohedral H@C60 complexes. Details of experimental work are presented, along with the results of simulations to investigate the process involved. The simulations are shown to be able to explain the experimental results.

Finally in chapter nine, the main results of the thesis are summarised and discussed. Ongoing work is described and possible future work is suggested.
Chapter 2

Molecular Dynamics Algorithms

2.1 Introduction

The basic algorithm used in conducting these ‘computer experiments’ is extremely simple. Indeed an MD program to calculate and display the position of particles moving under gravitational attraction that has been published is written in just 46 lines of BASIC [56]. On the other hand, programs written to obtain physically meaningful and useful data by MD simulation often require many thousands of lines of highly optimised code. There are three main reasons for the vast increase that is required in the complexity of the program. The size of a system that can be modelled by MD on a computer is necessarily finite (and extremely small), this gives rise to two of the problems to be overcome when conducting simulations. As the properties that are being investigated in the simulation generally belong to real systems that are orders of magnitude larger than those being simulated, results may be severely affected by the system size. Artificial means are sometimes applied to make the simulation behave as if it were part of a much larger system, e.g. atoms within the system or at its boundary may have their motion damped, or their temperature controlled to model energy dissipation from the simulated region to the adjoining material. In an attempt to increase the size of systems that can be described, many algorithms have been produced that take advantage of the nature of interactions within the simulation to increase the speed of the calculation. Bookkeeping methods such as neighbour-lists are used to prevent searches over the whole of system by keeping track of atoms which are interacting, whilst tabulation and interpolation can be used to reduce the time taken to evaluate complicated functions. The whole purpose of doing the simulation is to generate new information and so algorithms must be written to extract this from the mass of numerical data produced by the program. This can be done by analysing the data to produce numerical and statistical results, e.g. sputtering yields or displacement profiles. An increasingly used tool is data visualisation that allows static or moving images of the simulation to be produced. Being able to ‘see’ what is happening within the simulation can both increase the intuitive understanding of the dynamics and also reveal processes that would otherwise go unnoticed.
2.2 The Basic Classical MD Algorithm

2.2.1 Introduction

The basic scheme for conducting classical molecular dynamics is shown in figure 2.1. Starting from some given initial configuration, the evolution of the system is followed through time. As the equations of motion for the particles cannot be solved explicitly, their paths are numerically integrated. The history of the simulation is discretised so that the continuous evolution of the system becomes a sequence of finite steps forward in time. If the system is Hamiltonian, the interactions being simulated are modelled by a potential that gives rise to forces on the atoms; in classical MD this potential is represented as a functional of the positions of atoms within the system. Additional forces are applied in dissipative systems to model damping, heat conduction or energy loss due to inelastic collisions.

The simulations carried out in this thesis involve up to $10^6$ particles, whilst simulations with more than $10^8$ atoms have been conducted on massively parallel computers. The dimensions of a system that can be simulated are therefore measured on the scale of Ångstroms or nanometers. As phonon mode frequencies are of the order of $10^{14}$ Hz, the maximum time-steps that can be taken whilst accurately integrating trajectories are of the order of femtoseconds. This step-length is usually reduced to the order of tenths of femtoseconds to prevent high energy atoms from moving large distances in a single timestep. Typical simulations will involve several thousand timesteps, taking them into a range of picoseconds. These constraints of size and time restrict the energy range that can be simulated. The effects of high energy collisions travel further, so a larger system is necessary to prevent disturbances from reaching the edge of the simulated region. Simulation times are also increased as a longer time is taken for energy to dissipate from regions of high concentration and become thermalised. For example, when simulating ion bombardment of metals at energies between 1 keV and 10 keV, Doan et al. [57] required systems containing between 55296 and 175712 atoms, with simulation times of up to 10 ps necessary for the full evolution of collision cascades. Due to these constraints, most molecular dynamics simulations are limited to initial energies of up to tens of keV.
2.2.2 The Computational Box

The system to be simulated is initially constructed within some region of
three dimensional space. For simplicity a rectangular system is usually chosen,
although there is no real restriction on its shape. At the beginning of the
simulation all properties (position, mass, velocity, etc.) of every particle within
the system are specified. In the simulations described with this thesis, the crystal
lattice is generated by an algorithm based on the geometry of the crystal structure
as this allows a crystal of a specific size and orientation to be constructed
automatically. In the case of reconstructed or hydrogen terminated surfaces, the
minimum energy configuration was first obtained by annealing a structure where
atoms were initially in their approximate positions. A cell several layers deep,
containing the energy minimised structure of one surface unit was stored. When
conducting simulations, this cell is tessellated to make a surface of the desired
size, which is matched to the bulk material if a deeper lattice is required. Similarly, the C\textsubscript{60} molecule is read in from a file containing the minimum energy structure with respect to the interatomic potential function being used. At present algorithms to construct graphite, bulk diamond-structure lattices, 1 hydrogen monolayer terminated and bare reconstructed Si\{100\}(2×1) surfaces, 2 hydrogen monolayer terminated Si\{100\} surfaces, bulk and chain-fold terminated polyethylene crystals, fullerenes, dodecahedrane and C\textsubscript{100}H\textsubscript{60} have been produced.

2.2.3 Boundary Conditions

Depending on the type of simulation being carried out, different types of boundary conditions are applied to the surfaces of the computational box. Either free boundaries, periodic boundaries, or some combination of the two are routinely used. For simulations investigating sputtering, free boundaries are usually used as this allows atoms (and hence energy) to escape from the sides of the box. If periodic boundary conditions were used with the same sized target, atoms could re-enter the damaged region, leading to an incorrect calculation of the sputtering yield. Alternatively, simulations of fluids require periodic boundary conditions in all directions to contain the particles; this minimises edge effects that would dominate if reflecting boundaries were used.

Most of the simulations described in this thesis are concerned with the interaction of atoms or molecules with crystal surfaces. In these cases periodic boundary conditions are usually applied to the sides of the box to prevent reconstruction at the edges of the target and to prevent deposited molecules from escaping from the simulation. Free boundary conditions are applied in the vertical direction. On some occasions, free boundary conditions have been applied to all surfaces to prevent wave type motion from transferring energy through the boundary from one side of the system to the other. Periodic boundaries have been applied to all surfaces when simulating a region within a crystal. A problem associated with applying periodic boundary conditions is that although linear momentum is conserved, the total angular momentum of the system changes when an atom crosses a boundary of the system. This is of little concern in the simulations presented in this thesis, as the majority of atoms are bound within a crystal lattice. Whatever type of boundary conditions are used within the simulation, it is always necessary to ensure that a large enough system is being simulated so that any effects of the boundaries are minimised.
2.2.4 Potential and Force Calculations

In classical molecular dynamics, interactions between atoms are modelled in terms of potential energy functions that give rise to interatomic forces. The potential energy of the system can be divided between the atoms within the simulation, although the choice of how to assign the energy is usually arbitrary. If a pairwise potential is being used, then half of the energy due to each interaction can be attributed to each of the two atoms involved. This assignment of energy is not so easy to achieve in general for three-body or many-body potentials. For potentials such as those of Tersoff [13], where the energy of a bond is expressed as a pair term modified by a many body term, the same approach as with purely pairwise potentials can be used. Once the bond energy has been calculated, half the energy is assigned to the two atoms involved in the bond. The potential energy function is usually written as a function of the atomic positions. The force on an atom is given by the differential of the total potential energy of the system with respect to the position of that atom. The total potential energy of the system, and the force on atom $i$ can be written as

$$V = V(r_1, r_2, \ldots r_n)$$
$$F_i = -\frac{\partial V}{\partial r_i}$$ (2.2.1)

where $V$ is the potential, and $r_i$ and $F_i$ are the position of atom $i$ and the force it experiences. For the majority of empirical potential functions, the force can be calculated by an analytical expression for the derivative of the potential. This is the case for all potential functions used in this thesis, except for the proximity cell potential [58] detailed in section 3.5, which must be numerically differentiated.

In most situations it is the calculation of the forces experienced by atoms that requires the majority of the computer time, e.g. in the simulations described in this thesis over 90% of the computation was devoted to force calculations. If the calculated forces are identically zero beyond a certain short-ranged separation, then methods can be employed to exploit this feature. The efficient evaluation of long-ranged potentials is harder to achieve, but methods have been developed for certain situations [59].

21
2.2.5 Integration

The particles are assumed to move according to Newton's laws of motion, i.e. they behave as classical particles. For a system of \( n \) particles this can be written as

\[
\frac{dr_i}{dt} = v_i, \quad i = 1,...,n
\]

\[
m_i \frac{dv_i}{dt} = F_i
\]

where \( m, r, v, \) and \( F \) are the mass, position, velocity and force associated with atom \( i \). Hence, once the force on each atom has been calculated, all velocities and positions can be updated using a suitable numerical integration scheme.

2.3 Efficient Evaluation of Forces

2.3.1 Introduction

The most computationally expensive procedure during MD simulation is the evaluation of the forces acting upon the atoms in the system. As the MD technique has developed, many schemes have been proposed to reduce the time taken by force evaluation. These methods may be divided into two categories. One set of methods reduces the number of force evaluations that are actually required, e.g. neighbour lists are used to keep track of atoms which are interacting. Other methods are concerned with increasing the efficiency of the force evaluations that are carried out, e.g. tabulation and interpolation can be used to replace the evaluation complicated functions. The latter methods are specific to the potential function that is being evaluated, while all methods are dependent to some extent on the specific machine on which the program is run. Several methods of increasing the efficiency of MD simulations using empirical many-body potentials on single workstations have been examined.

In particular, three methods of producing neighbour lists have been compared. The optimal size of the neighbour list has been established, along with a method of infrequently updating the neighbour information. Timing information obtained from simulations using these algorithms is presented.
2.3.2 Evaluation of Potential Functions

The size of the system that can be simulated is dependent upon the speed with which the potential and forces can be evaluated. The goal in producing empirical potentials is therefore to create a functional that is relatively simple to evaluate and differentiate and that can be parameterised to accurately model the chemical and physical properties of one or more elements. If the interaction between atoms rapidly decays as their separation is increased, it can be assumed to be zero for all distances greater than some cutoff distance. This is the case for materials that combine via metallic or covalent bonds. In the case of the covalent materials studied in this thesis, the interactions are assumed only to involve nearest neighbours in the crystalline forms of the material. A cutoff function is applied to all interactions to reduce them smoothly to zero before the second neighbour distance. The immediate consequence of this is that each atom only interacts with a small number of adjacent atoms. Hence the number of interactions that must be calculated for each atom is independent of the total number of atoms in the system. The algorithms described below all assume that all interactions reduce to zero at a distance that is small compared to the edge length of the computational box.

To avoid the calculation of complicated mathematical expressions, tabulation of potentials has been applied to increase the speed of calculations [60]. Instead of evaluating a function, table look-up is used obtain the potential and forces. This works well for pair potentials, where the potential and force between two atoms can be tabulated as functions of the square of the distance between them. Interpolation is usually used to reduce the error from table look-up, but if enough memory is available, spacing between tabulation points can be reduced to the extent that interpolation is not required. There is little advantage in using tabulation when many-body potential functions such as those utilised in this thesis are required. As many-body potentials generally consist of several different functions, each of which would have to be tabulated separately, a large amount of memory would be required to store the tables and a considerable proportion of the computation time would be devoted to accessing memory. The advent of efficient math co-processors means that the speed of direct evaluation is comparable to that of table look-up, especially if interpolation is required. Much of the time devoted to force evaluation is spent assigning values to various arrays or temporary variables and doing unavoidable calculations of multiplication and addition. For example, with the Tersoff-type potentials used in this thesis, only a quarter of the time is spent evaluating functions that could be tabulated. Direct evaluation has therefore been used with all potentials, as its accuracy is greater than look-up.
This also leaves the maximum amount of memory available for storage of positions, velocities and other atomic properties and so allows larger simulations to be conducted.

2.3.3 Neighbour-List Methods

If a short-ranged potential is being used to model interactions in the system, only interactions between closely separated atoms are calculated. However, at each stage in the calculation of the potential function, every possible interaction has to be checked to see if atoms are within interaction distance. So the calculation has a component that scales as \( N^2 \), where \( N \) is the number of atoms in the system. This checking will quickly swamp the calculations, especially in the case of many-body potentials, where several different interactions between each pair of atoms may be calculated at each timestep.

To reduce the amount of checking required a list of neighbours within a cutoff distance can be created for each atom [6]. When potential and force calculations are carried out, the only interactions that need to be considered for each atom are between it and those atoms in its neighbour-list. Hence the force calculation is \( O(N) \) and the amount of checking is minimised, but at the expense of additional storage and retrieval of the neighbour information. The problem is then how to efficiently create and store the neighbour information. In systems containing more than one element, interactions will cutoff at different distances depending on the types of the atoms involved. A different cutoff distance can be used for each type of interaction to minimise the list size.

Three alternative methods of updating the neighbour information are compared here. The three methods are: (i) The Verlet-list [6], (ii) The Method of Lights [61], (iii) The Coarse Grained Cell [60,62] (also known as the linked list method). The methods are of varying complexity and to an extent, the efficiency of the three methods is dependent upon the computer architecture being used. To obtain an estimate of the efficiency of these three methods in creating neighbour lists for use with short ranged potentials, the following assumptions are made for a system of \( N \) atoms: (i) All interactions cut off at a distance \( R \), (ii) The average density of the atoms is \( D \), (iii) The system is large enough so that any boundary effects are negligible, (iv) The time taken to find the distance between a pair of atoms and check if it is less than \( R \) is a constant, denoted by \( C \), (v) The time taken to add one neighbour to the list is a constant, denoted by \( A \).

In the original method introduced by Verlet [6], the distance between each atom and all other atoms in the system is checked, and any atoms within the cutoff distance are stored. A schematic representation of the method for one atom
in a two-dimensional system is given in figure 2.2. As the distance between any two atoms only needs to be found once \( \frac{1}{2}N(N-1) \) checks must be carried out. For each atom, on average \( \frac{1}{2}\pi R^2 D \) neighbours will be added to the list. The total cost of one application of the method is \( \frac{1}{2}CN(N-1) + \frac{1}{2}A\pi NR^3 D \), and so the algorithm is \( O(N^2) \).

![Figure 2.2. Schematic representation of the Verlet-list method. To construct the neighbour-list for one atom, the distances between it and all other atoms are calculated and any atoms within the sphere of radius \( R \) are stored.](image)

The Method of Lights algorithm [61] was developed to take advantage of the capabilities of vector processing computers, but can be efficiently applied on scalar machines. The atoms are indexed in order in the directions of the three axes, and the neighbours furthest away but within the cutoff are determined for each atom in each direction. Although each of these operations requires a sort to be completed, the results of the previous call of the routine will still be in almost sorted order and so the operation will be practically order \( N \) [63]. This cost is therefore \( 3SN \) where \( S \) is the cost of a sort and determining limits in one direction per atom. Atoms are then examined in the order of increasing \( x \) co-ordinate and their neighbours are determined. For each atom, it is already known which atoms lie within range in the \( x \) direction, but these atoms must be checked in the \( y \) and \( z \) directions to see if they are within the cutoff distance. This checking is efficient as atoms have been indexed and their bounding atoms found in these directions. For a possible neighbour to be within the cutoff distance, the atom must lie between its bounding atoms in both directions. The method is illustrated schematically in figure 2.3. Assuming the system to be a cube with volume \( V \), then the volume of a
slice 2R thick is $2R\sqrt{2}$, i.e. it contains $2RN\sqrt{2}$ atoms. If the cost of checking the limits on one possible neighbour is $B$, the total cost per atom will be $B2RN\sqrt{2}$, but in practice only half the checks have to be made. The atoms within a box of side 2R are possible neighbours, but the size of the neighbour-list can be significantly reduced by considering the distance between atoms. There will be on average $8R^3D$ possible neighbours per atom, but at the expense of $4R^3D$ checks on distance this can be reduced by almost 50% to $\frac{1}{2}R^3D$. The total cost of the algorithm is then $3SN + BRN\sqrt{2} + 4CNR^3D + \frac{1}{2}\pi ANR^3D$, i.e. the algorithm is $O(N^{60})$.

Figure 2.3. Schematic representation of the Method of Lights algorithm. For each atom between the x direction bounding atoms (labelled XL and XU) of atom i (the atom coloured black), a check is made to see if atom i lies between their y and z direction bounding atoms. The resulting list contains the dark grey atoms, but a check on distance reduces this to the atoms lying within the sphere.

The third method to be examined was the Coarse Grained Cell Algorithm, this method is also known as the Linked List algorithm due to the efficient method of storing neighbour information. The computational box (with sides of length $L_x \times L_y \times L_z$) is divided into an $M_{xyz} = M_x \times M_y \times M_z$ grid of rectangular cells whose sides exceed $R$. An atom can then only interact with atoms in its cell or in the surrounding layer of cells. Each cell then has sides of length $\omega_x \times \omega_y \times \omega_z$, where $\omega_i = L_i / M_i$ and $i = x, y$ or $z$. It is optimal to have as few atoms in each cell as possible, hence $M_i$ is taken as the largest integer $\leq L_i / R$. 
Building the cell-list is equivalent to performing a sort in each direction, giving a cost of $3SN$. For each atom, its cell and all 26 neighbouring cells contain possible neighbours, but only half need to be considered as illustrated in figure 2.5. The size of the neighbour lists is minimised by calculating the distance to these possible neighbours. This reduces the size of the list by a factor of 6.45 (from $27R^3$ to $\frac{2}{3}\pi R^3$), but there are $\frac{1}{2}27R^3 D$ checks to be made on distance per atom. With additions to the list, this method then costs $3SN + \frac{1}{2}27CNR^3 D + \frac{1}{2}\pi ANR^3 D$. Another variant of this method that has not been investigated here involves using cells with a smaller edge length than the cutoff distance [64]. In addition to immediate neighbours, other cells will have to be checked when constructing the neighbour-list, but as the cell size is reduced, the volume of the cells that must be checked becomes approximately spherical. This removes the need to apply any checks on the distance between atoms.

The cell list algorithm lends itself most readily to the application of periodic boundary conditions. It can be extended to free boundary conditions by making all cells on the surface of the computational box infinite in directions away from the box. As the cells are fixed in space, care must be taken to ensure movement of large molecules or sputtering does not result in some of these surface cells containing far more atoms than the average number.
The order of the methods is $N^2$, $N^{5/2}$ and $N$ for the Verlet, Method of Lights and Linked List algorithms, respectively. For large systems, the Linked List algorithm will be the most efficient, but one of the other methods could be the most efficient for simulations of smaller systems. To investigate the efficiency of the algorithms, simulations were run using all three algorithms with a test system of varying size. The simulation chosen was that of collision between normally incident $C_{60}$ and a diamond {111} surface. The sizes of system examined are shown in table 2.1. For each system size, the energy of the $C_{60}$ was chosen to be near the maximum energy that could be realistically simulated. Except for the different neighbour-list routines, the simulation programs were identical, with the only changes being the system size and the impact energy of the fullerene. All the simulations were run on the same 35 MHz SUN Sparc-10 for 1 ps, using an integration timestep of 0.2 fs. The time per call of each neighbour-list routine was obtained by using the standard UNIX profiling tools.

The points on the graph in figure 2.6 are timing results from the simulations described in table 2.1. The curves are lines of the form $T = cN^m$, where $m$ is either 1, 5/2 or 2 and $c$ was fit to the last data point displayed for each algorithm. If the equations given for these fits are assumed to be accurate for all $N$, then the Coarse Grained Cell algorithm is the most efficient for large $N$, the Method of Lights is more efficient if $N < 1128$ and the Verlet algorithm is more efficient than the Method of Lights only for $N < 2$. As most systems that will be simulated contain over 2000 atoms and the Linked List algorithm is clearly more efficient for systems of this size, it has been used in all subsequent simulations.
<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Breadth (Å)</th>
<th>Width (Å)</th>
<th>Depth (Å)</th>
<th>N (atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>15</td>
<td>15</td>
<td>4</td>
<td>258</td>
</tr>
<tr>
<td>50</td>
<td>25</td>
<td>25</td>
<td>4</td>
<td>640</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>30</td>
<td>5</td>
<td>1110</td>
</tr>
<tr>
<td>250</td>
<td>37</td>
<td>37</td>
<td>7</td>
<td>2145</td>
</tr>
<tr>
<td>500</td>
<td>50</td>
<td>50</td>
<td>8</td>
<td>4200</td>
</tr>
<tr>
<td>1k</td>
<td>58</td>
<td>58</td>
<td>9</td>
<td>6407</td>
</tr>
<tr>
<td>2k</td>
<td>58</td>
<td>58</td>
<td>15</td>
<td>10215</td>
</tr>
<tr>
<td>5k</td>
<td>58</td>
<td>58</td>
<td>28</td>
<td>17831</td>
</tr>
<tr>
<td>10k</td>
<td>70</td>
<td>70</td>
<td>38</td>
<td>34108</td>
</tr>
<tr>
<td>20k</td>
<td>100</td>
<td>100</td>
<td>54</td>
<td>99420</td>
</tr>
</tbody>
</table>

Table 2.1. The test cases used to examine the efficiency of algorithms for producing neighbour-lists.

Figure 2.6. Timing results for neighbour-list update.

2.3.4 Infrequent Neighbour List Update.

The time taken updating neighbour lists can be reduced by an order of magnitude if an update is only carried out once every few time-steps. This is achieved by storing all atoms that are within the cutoff distance plus some skin thickness. It is only necessary to update neighbour lists if the relative distance
travelled by two atoms is greater than this skin thickness. At each time-step the two largest displacements are added to an accumulator, and the list is updated when this sum is greater then the skin thickness.

![Figure 2.7. Neighbour list using an additional skin to reduce the update frequency.](image)

To determine the optimum skin thickness for use with the linked-list algorithm, simulations were run for the set of test trajectories given in table 2.1, with various values used for the skin thickness. As additional atoms are included in the neighbour list, the potential and force evaluation routine will have to deal with redundant atoms. The way that this is achieved is detailed in section 2.3.5. A skin thickness of around 0.75 Å was found to be optimal. As cutoff distances are around 2 Å, this more than doubles the size of the neighbour-list, but updates are only required approximately once every twenty time-steps. Using this size of neighbour-list, the time taken to generate the list is about the same as that for one set of force evaluations with a many-body potential.

2.3.5 Data structure

To avoid unnecessary checking of distances, a pair of atoms can be simultaneously added to each others neighbour list if they are with the neighbour list radius. To accomplish this efficiently, we have developed the following data structure. The neighbour list is stored as a linked-list rather than an array, and information concerned with the use of periodic boundaries is also stored within the list. Hence each place in the list contains three elements; the neighbour, the type of boundary associated with the neighbour and a pointer to the next neighbour. The definition of the boundary type is given in figure 2.8 for the case
used in most simulations in this thesis; periodic boundaries are applied in the $x$ and $z$ directions, with free boundaries applied in the $y$ direction. If the vector between two atoms does not cross the boundary of the computational box, both $\Delta X$ and $\Delta Z$ are zero, otherwise they can take values of 1 or -1 depending upon which boundary is crossed.

![Figure 2.8. Definition of boundary types.](image)

The boundary type for the $j$th neighbour of atom $i$ is given by

$$BTYPE_{ij} = 3 \times \Delta X + \Delta Z$$  \hspace{1cm} (2.3.1)

and so can take values from -4 to 4. In the case shown in the diagram, $BTYPE_{ij} = -4$. The algorithm to construct the neighbour-list is then the following.

Zero all neighbour lists

Loop through all atoms

LOOP

Zero the neighbour-list for this atom; NEBPNT(I) points to the first neighbour of atom $i$, or to NULL if $i$ has no neighbours

NEBPNT(I) = NULL

ENDLOOP

Zero the total neighbour-list; LSTPNT points to the last neighbour in the list, or to NULL if the list is empty

LSTPNT = NULL

Check each pair of atoms that may be in neighbour radius

Only check each pair of atoms once

Loop through all pairs of atoms that may be within the neighbour radius
LOOP I & J

Record if any vector crosses an edge of the box w.r.t atom i
EVALUATE ΔX
EVALUATE ΔZ
Check if atoms are within radius, allowing for periodic boundaries
EVALUATE RIJ

If within radius
IF RIJ < RAD

Get boundary type
BTYPIJ = 3 * ΔX + ΔZ

Add atoms to each others neighbour-lists

Add j as a neighbour of i
Extend the list by one
LSTPNT = LSTPNT + 1
Add j
NEBOUR(LSTPNT) = J
Add j’s boundary-type relative to i
PBCTYP(LSTPNT) = BTYPIJ
Make j the first atom in i’s linked-list of neighbours
POINTR(LSTPNT) = NEBPNT(I)
NEBPNT(I) = LSTPNT

Add i as a neighbour of j
LSTPNT = LSTPNT + 1
NEBOUR(LSTPNT) = I
PBCTYP(LSTPNT) = -BTYPIJ
POINTR(LSTPNT) = NEBPNT(J)
NEBPNT(J) = LSTPNT

ENDIF

ENDLOOP
The list is used for the evaluation of the potential function, analysis of the distribution of molecules and to output data. The algorithm to read the list is

Set up offsets for periodic boundary conditions for BTYP<sub>e</sub> from -4 to 4

```plaintext
LOOP BTYPIJ
    X(Z)OFFSET is either -LX(Z), 0, or +LX(Z)
    XOFFSET(BTYPIJ) = LX * (INT((BTYPIJ+4)/3) - 1)
    ZOFFSET(BTYPIJ) = LZ * (MOD((BTYPIJ+4), 3) - 1)
ENDLOOP
```

Loop through all atoms

```plaintext
LOOP I
    Get the place in the list of the first neighbour of i
    LSTPNT = NEBPNT(I)

    WHILE LSTPNT != NULL
        Find the neighbour atom and its boundary type
        J = NEBOUR(LSTPNT)
        BTYPIJ = PBCTYP(LSTPNT)

        Find position in the list of the next neighbour of i
        LSTPNT = POINTR(LSTPNT)

    Find the internuclear vector and the distance between the atoms
    XOFFSET and ZOFFSET remove multiples of the box-lengths (LX & LZ) to get the correct internuclear vector when atoms are interacting over a boundary
    RXIJ = RX(J) - RX(I) - XOFFSET(BTYPIJ)
    RYIJ = RY(J) - RY(I)
    RZIJ = RZ(J) - RZ(I) - ZOFFSET(BTYPIJ)
    RIJ2 = RXIJ*RXIJ + RYIJ*RYIJ + RZIJ*RZIJ

    See if the atoms are with cutoff distance
    IF RIJ2 < CUTIJ2
        Atoms i and j will interact
    ENDIF

ENDWHILE
```

ENDLOOP
2.3.6 Many-Body Potentials

The simulations described in this work use many-body empirical potential functions such as Brenner's hydrocarbon potential [65], to describe interactions in covalent systems. These Tersoff-type potentials are evaluated as a sum over bonds. The potential energy of a bond between atoms \( i \) and \( j \) is dependent upon all atoms that are first or second neighbours of \( i \) and \( j \), as illustrated schematically in figure 2.9.

![Figure 2.9. The energy of bond \( i-j \) is dependent upon the positions of \( i, j \) and their 1st and 2nd neighbours.](image)

Many terms in the potential function are pairwise, such as the bond length and its direction cosines, and the cutoff function and its derivative. These terms are required several times for each bond during the evaluation of the potential and forces. To increase the efficiency of the program, these terms can be evaluated once and then stored. In the implementation of the potentials used in this thesis, the potential evaluation is therefore split into two parts. The first component extracts information from the neighbour-list. The possible neighbours of each atom are found and the internuclear vector is calculated, taking into account the possibility that neighbours may exist due to periodic boundary conditions. Atoms that are included in the neighbour-list due to the use of a skin to allow infrequent update can be removed at this time. If the separation of the atoms is less than the cutoff distance all pairwise interactions are calculated and stored in a temporary list, otherwise the neighbour is ignored. The stored terms include the bond length, the components of the unit vector in the direction of the bond, and the value of cutoff function and its derivative. Any pairwise potentials and forces, such as the ZBL universal potential used to describe interactions with noble gas atoms in
bombardment simulations, are also calculated at this stage. The main potential and force calculations then use the terms stored in the temporary list, so checking for interaction or calculation of distance is not necessary. The only calculations that are required are for the many-body components of the potential.

2.4 Integration of Trajectories

2.4.1 Integration Schemes

The time evolution of a trajectory is followed by numerically integrating the paths of atoms within the system. Many different schemes of varying complexity have been proposed to carry out this integration, for example see references \[62,66,67\]. It is normal to use an explicit, low order integration scheme with a suitably small timestep as this gives the best combination of efficiency and accuracy. Many potential functions such as the Brenner potential only possess a continuous first derivative, with discontinuities in the second derivative. Hence, higher order integrators that assume a continuous value for the second and higher derivatives can actually be less accurate than a low order method. The acceleration \( \mathbf{a} \) of a particle is given by

\[
\mathbf{a} = \frac{1}{m} \mathbf{F} = -\frac{1}{m} \frac{d\mathbf{V}}{d\mathbf{r}}
\]  

(2.4.1)

where \( m \) is the mass of the particle, \( \mathbf{r} \) is its position and \( \mathbf{F} \) is the force experienced due to the potential \( V \). If the integrator is assumed to be explicit and require only one force evaluation per timestep it can be treated as a Taylor expansion of the form

\[
\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{v}_n \Delta t + \mathbf{a}_n \Delta t^2 + \mathbf{\ddot{a}}_n \Delta t^3 + \text{higher order terms} \\
\mathbf{v}_{n+1} = \mathbf{v}_n + \mathbf{a}_n \Delta t + \mathbf{\ddot{a}}_n \Delta t^2 + \mathbf{\dddot{a}}_n \Delta t^3 + \text{higher order terms}
\]  

(2.4.2)

where the positions, velocities and accelerations of a particle are represented by \( \mathbf{r}, \mathbf{v} \) and \( \mathbf{a} \) respectively, \( \Delta t \) is the length of the timestep (typically around 0.2 fs) and the subscripts refer to the timestep at which the variables are evaluated. The derivatives of the position are assumed to be continuous within the timestep. The derivative of the acceleration is given by

\[
\mathbf{\dddot{a}} = \frac{1}{m} \frac{d\mathbf{F}}{dt}
\]  

(2.4.3)
and therefore is only continuous if the second derivative of the potential is continuous. The usual form of the cutoff function in Tersoff-type potentials [13] is only continuous to the first derivative at its end-points. Although a similar function continuous to the third derivative has been produced, it has other drawbacks as shown in section 3.4.5. In any case, the cutoff function is not the only place in the potential where such problems occur. In the Brenner potential correction terms are included as cubic interpolation functions, fit to function and derivative values at given points. These too are only continuous to the first derivative. So in general for these type of potentials only the first derivative of the potential can be reliably used in numerical integration schemes. Truncating the Taylor expansions after this term leads to

\[
\begin{align*}
    r_{n+1} &= r_n + v_n \Delta t + a_n \Delta r_n^2 / 2 + O(\Delta r_n^3) \\
    v_{n+1} &= v_n + a_n \Delta t + O(\Delta t)
\end{align*}
\]  

(2.4.4)

As the expression for velocity assumes a constant acceleration, a slight gain in accuracy can be expected by replacing the acceleration by its mean at the two time values, to give

\[
\begin{align*}
    r_{n+1} &= r_n + v_n \Delta t + a_n \Delta r_n^2 / 2 + O(\Delta r_n^3) \\
    v_{n+1} &= v_n + [a_n + a_{n+1}] \Delta t / 2 + O(\Delta t^3)
\end{align*}
\]  

(2.4.5)

which is Verlet’s algorithm [6]. Note that the expression for velocity is only accurate to first order unless the potential does possess a continuous second derivative, in which case the expression is accurate to second order. Verlet’s method also has the advantage that it is symplectic [68], i.e. it is accurate in preserving all the Hamiltonian invariants. It is the only one-step integration method that is symplectic.

All potential functions possess a continuous first derivative, and most have several derivatives that are piece-wise continuous. For the Tersoff-type potentials used in this thesis, discontinuities occur in the second derivative due to the use of interpolation functions; either as a cutoff function, or as some type of ‘spline’ as a correction term where the functional form is not known. There is no practical reason why these functions cannot be reformulated to possess continuous second and higher derivatives, but finding an efficient method that increases the accuracy of the simulation is difficult. These matters are discussed in more detail with regard to the Tersoff cutoff function in section 3.4.5. As most potential functions possess several derivatives that are piece-wise continuous, higher order methods
can sometimes be used to increase accuracy of simulations if the discontinuities are not crossed very often. This is the case if a solid is being modelled using Tersoff’s potential, where the only discontinuity is in the cutoff function. The problem only becomes apparent if the potential is used to model a liquid or gas where atoms are continuously passing through the cutoff region.

In high energy simulations, atoms approach each other close enough so that they are in the repulsive part of the potential. Here the forces are large and change rapidly with distance, so a higher order method can give greater accuracy. A scheme such as the third order algorithm developed by Smith and Harrison [66] shown in equation (2.4.6) can be used.

\[
\begin{align*}
    r_{n+1} &= r_n + v_n \Delta t + \left[4a_n - a_{n-1}\right] \Delta t^2/6 + O(\Delta t^4) \\
    v_{n+1} &= v_n + \left[5a_n + 8a_{n-1} - a_{n-2}\right] \Delta t/12 + O(\Delta t^4)
\end{align*}
\]  (2.4.6)

This uses an Adams-Bashforth expression for the position and an Adams-Moulton expression for the velocity. The higher order of the method is achieved by estimating higher derivatives of the forces by central and forward differences of the acceleration. This creates a small overhead of extra computation and requires extra storage for the acceleration of the past two timesteps, but this is compensated for by the increased accuracy or slight increase in timestep that is gained.

2.4.2 Variable Timesteps

For high energy simulations such as keV ion bombardment, the velocities of the particles vary widely as the simulation progresses. Some atoms will initially have very high energies, but as the energy of the ion is transformed into thermal motion of the target atoms, all atoms will achieve similar low energies. The size of the time-step taken can be automatically adjusted within the program to ensure a good combination of speed and accuracy is achieved. The variable timestep version of the Smith and Harrison scheme is

\[
\begin{align*}
    r_{n+1} &= r_n + v_n \Delta t_n + \left[(3+R)a_n - Ra_{n-1}\right] \Delta t_n^2/6 \\
    v_{n+1} &= v_n + \left[(3+2R)a_{n+1} + (3+R)a_n - R^2a_{n-1}\right] \Delta t_n/6
\end{align*}
\]  (2.4.7)

where $R$ is the ratio of the present and the previous timesteps.
The usual method applied in the choice of time-step is to make the maximum distance moved by an atom equal to some given value. The time-step is then given by

$$\Delta t_n = \frac{C_{\text{DIS}}}{\max_{i=1,N} (|v_i|)}$$

(2.4.8)

where $v_i$ is the velocity of atom $i$ and $C_{\text{DIS}}$ is a constant that will depend upon the system being simulated, but usually has a value of the order of 0.1 Å. For high energy simulations the potential energy term is important, as atoms may be moving slowly but have high potential energies during impacts. We have found an extension of the above method gives improved accuracy. The chosen method of selecting the timestep is via the formula

$$\Delta t_n = \frac{C_{\text{DIS}}}{\max_{i=1,N} \left( 2 \times \left[ \frac{KE_i + \max(0, PE_i)}{M_i} \right] \right)}$$

(2.4.9)

where $KE_i$ and $PE_i$ and $M_i$ are the kinetic energy, potential energy and mass respectively of atom $i$. The method is dependent upon an expression being available for the potential energy of an atom, which is not always the case. However, for pairwise and Tersoff-type potentials this can be achieved in an unambiguous fashion as explained in section 2.2.4. Equation (2.4.9) reduces to the form of equation (2.4.8) when no atom has a potential energy greater than zero. To ensure that the accuracy of the simulation is maintained, the maximum displacement and the maximum change in the potential energy of each atom is calculated at each time-step. If either are above a specified tolerance, the atoms’ positions and velocities are reset and the step is retaken with a recalculated step size. A limit is also imposed on the maximum step-size that can be used by the method. When the timestep is increasing it has been found that a weighted sum of the previous and predicted timestep is useful, as it prevents rapid oscillations in the size of the timestep during high energy impacts. A weighted sum of the form

$$\Delta t'_n = \frac{3}{4} \Delta t_{n-1} + \frac{1}{4} \Delta t_n$$

(2.4.10)
that is dominated by the old timestep is required. This a negligible effect on the speed of the simulation as the time-step is still able to increase rapidly when the maximum energy of atoms decreases.

It should be noted that many other methods to increase the efficiency of simulations have been applied at different times. For keV particle bombardment of semiconductors, Smith, Harrison and Garrison introduced the 'moving atom approximation' [69]. In this scheme the system starts at 0 K with all target atoms on their lattice sites, and initially only the motion of the bombarding ion is integrated. The forces among the ion and its neighbours are evaluated and if the force on any neighbour is less than some threshold its motion is not integrated. If the force is greater than this threshold, the atom is 'turned on' and the forces among it and its neighbours are evaluated and its motion is integrated. As the simulation runs, more atoms become turned on as the energy of the ion dissipates through the target. Sayed [70] has extended this scheme so that the lattice is not even constructed until atoms are required for force evaluation, reducing the memory requirements of simulations. The 'moving atom approximation' is not suitable for general use in MD as it assumes a high energy collision with a lattice initially at 0 K. A more sophisticated algorithm has been put forward by Marqués et al. [71], where the motion of all atoms is integrated, but several timesteps are used. The smallest timestep is chosen, based on the highest energy atom and all atoms have a timestep that is some multiple of this, depending upon their energy. There is a significant overhead in calculating forces in this way, but if several timesteps can be used the overall effect is to improve the efficiency of the simulation. This is the case for high energy ion bombardment, where an acceleration of a factor of 5 was reported over a single adaptive timestep method.

Long-range potentials are generally used for modelling non-bonded interactions such as the Van der Waals forces between graphite layers or the interaction between individual polymer chains. As these interactions are weak and vary slowly with distance, a longer timestep can be used for their evaluation. Scully et al. [59] have examined this procedure and found a 60% reduction in computational time by using three different timesteps for interactions in different ranges.
2.5 Finite Temperature Simulations

2.5.1 Adding Temperature to the System

To enable simulations to be conducted starting at a finite temperature rather than at absolute zero, energy must be added to the system. This energy will be equipartitioned between the kinetic energy of atoms due to thermal motion and a raise in the potential energy due to displacements from equilibrium positions. The simplest method of adding heat is therefore to add twice the desired energy as kinetic energy of the atoms and allow the system to equilibrate. To reduce the time taken in equilibration, the energy can be added directly as a combination of kinetic and potential energy.

The scheme developed for use in the work presented here is shown in figure 2.10. The system is first constructed at zero K and then atoms are assigned displacements and velocities according to Gaussian distributions. The approximate average displacement of atoms is calculated according to the temperature and the average radius of the atom. These displacements are then uniformly scaled until the correct rise in the potential energy of the system is achieved. The thermal velocities of the atoms are assigned in a similar way and the system is allowed to equilibrate for around 100 fs. After equilibration, the relative velocities are added between the projectile and the target and the simulation is started.

2.5.2 Temperature Control

During the collision of a molecule or ion with a crystal surface a considerable amount of kinetic energy is transferred to the target. This energy is then transformed into thermal motion of the atoms in the target material. In a real collision, this thermal energy would disperse away from the impact point into the bulk of the target. As the region being simulated is extremely small, this cannot happen and the energy remains trapped around the impact point leading to an unnaturally high temperature in the target. Several methods have been developed to control the temperature of atoms. Velocity scaling to correct the temperature either at every step, or infrequently has been used by several authors [72]. Other workers have employed stochastic methods to control the temperature [73]. These methods and many other methods of temperature and pressure control are described in reference [74].
Specify temperature, $T$ (K)

Calculate the average kinetic energy of atoms
$KE = \frac{3}{2}kT$ (k is the Boltzmann constant)

Guess the average displacement of atoms in each direction
$DIS = \sqrt{T/60000.0}$
$D = DIS \cdot RAD/\sqrt{3.0}$

Guess the average velocity of atoms in each direction
$V = \sqrt{KE/(1/2 \cdot MASS \cdot \sqrt{3.0})}$

Construct the system at zero $K$
Find the zero $K$ potential energy of the system

Calculate random displacements
$DX = D \cdot GAUSS$

Calculate potential energy of system with displaced atoms

Scale displacements to give correct potential energy

Calculate random velocities
$VX = V \cdot GAUSS$

Scale velocities to add rest of energy as kinetic energy

Let system equilibrate for a short time

Figure 2.10. Schematic diagram of the heater algorithm.
The method used in this thesis when temperature control is required is that of Berendsen et al. [74], where atoms are weakly coupled to an external bath. At every timestep, velocities of all atoms coupled to the bath are scaled by

$$\lambda = \left[ 1 + \frac{\Delta t}{\tau} \left( \frac{T}{T_0} - 1 \right) \right]^{\gamma_0}$$

(2.5.1)

where $\Delta t$ is the timestep, $T$ is the present temperature and $T_0$ is the reference temperature. The time-constant $\tau$ represents the strength of the coupling between the system and the bath. The minimum value recommended for $\tau$ by Berendsen is 0.1 ps, and larger values give weaker coupling. The advantage of this method is that it is simple to implement. It is trivial to couple only some of the atoms to the bath, e.g. in simulations involving a crystal surface, only boundary and base atoms are coupled to model the transfer of energy into the bulk. The reference temperature can be altered during the simulation if required and the strength of the coupling can also be altered, e.g. to anneal or quench a configuration of atoms.

2.6 Selection of Representative trajectories

To obtain statistical data from simulations for comparison with experiment, many simulations have to be conducted using slightly different initial conditions. For example, to calculate the average sputtering yield per ion impact with a specific impact velocity requires sampling as the impact point is varied over a representative area of the crystal surface. The representative area is usually the smallest unit that can be periodically repeated to produce the complete surface. Thus to increase the accuracy of the predictions, the representative area must be sampled as uniformly as possible, but not so regularly as to allow any possible correlation between the lattice structure and the points sampled. To achieve this, the impact positions can be chosen via the Halton sequence [75].

The Halton sequence generates a quasi-random set containing an arbitrary number of $n$-dimensional points within some unit hypercube. It is constructed to reduce the error in Monte-Carlo integration of the volume of a hyperbrick within the unit hypercube. Thus it gives a more even distribution of points than selection purely at random, while maintaining a type of randomness. By choosing the dimension of the hypercube to be two, a good selection of points within the representative area can be obtained. The Halton sequence has the advantage over the similar Hammersly sequence [76] that the number of sample points does not have to be specified at the beginning of the simulations, i.e. more trajectories can be computed to increase the accuracy of the computed result if required.
2.7 Analysis of Simulation Results

During ion bombardment of materials, atoms and molecules are sputtered from the surface and if the target is a molecular crystal, its constitution will be altered. We have developed a recursive algorithm to analyse the distribution of molecules in these situations. Each atom is examined in turn and if it has not already been allocated to a molecule, a new list is initiated and a molecule building routine is called. This recursive routine adds all bonded neighbours of the atom that are yet to be allocated to a molecule to the list of atoms within the molecule, calls itself for all these atoms then returns. A definition of bonding between atoms is required by the algorithm. A suitable criteria to determine the existence of a bond between atoms is based on the cutoff function used for each type of interaction. This function is unity for close separation of atoms and decays to zero at some cutoff distance; atoms were assumed to be bonded if the value of this function was greater than 0.5. Of course this does not define a stable molecule, but gives a snapshot of which atoms are interacting at any time. As a test for sputtering, a molecule is deemed to be ejected if all its constituent atoms are above the original crystal surface.

The version of the program to analyse the distribution of hydrocarbon molecules produced by the ion bombardment of polyethylene is illustrated below.

Set up array to count number of \( C_xH_y \) molecules

\[
\text{LOOP NC & NH}
\]

Zero the number of sputtered or lattice \( C_xH_y \) molecules

\[
\text{NSCXHY (NC, NH) = 0}
\]

\[
\text{NLCXHY (NC, NH) = 0}
\]

ENDLOOP

Find which neighbours are within the 'bond' distance of each atom

Loop through all atoms

\[
\text{LOOP I}
\]

Loop through all neighbours and find which are 'bound'

\[
\text{LOOP J}
\]

\[
RIJ2 = RXIJ*RXIJ + RYIJ*RYIJ + RZIJ*RZIJ
\]

Check if atoms are 'bound'

\[
\text{IF RIJ2 < BNDIJ2}
\]

Add \( j \) to the list of atoms bound to \( i \)

ENDIF
Label all atoms as unchecked
FOUND(I) = FALSE

Check all atoms and label those above the crystal surface
IF RY(I) < 0.0
    SPUTT(I) = TRUE
ELSE
    SPUTT(I) = FALSE
ENDIF

Routine to find molecules

Loop through all atoms
LOOP I

Make sure this is an unallocated atom
IF NOT FOUND(I)

This is the first atom in a new molecule
Initiate a list with atom i as its first entry
NLIST = 1
BNDLST(NLIST) = I
Record that atom i has now been allocated to a molecule
FOUND(I) = TRUE

Build the molecule containing this atom
CALL BONDED(BNDLST, NLIST)

Now analyse the new molecule

Zero the number of C and H atoms within the molecule
NC = 0
NH = 0
Assume the molecule is sputtered, and check later
SPIMOL = TRUE

Loop through all atoms in this molecule
LOOP N
Get the n’th atom in the molecule
J = BNDLST(N)
If this atom is not above the surface, the molecule is not sputtered
IF NOT SPUTT(J)
    SPIMOL = FALSE
ENDIF
Increment the number of C or H atoms in the molecule
IF TYPE(J) = CARBON
    NC = NC + 1
ENDIF
IF TYPE(J) = HYDROGEN
    NH = NH + 1
ENDIF
ENDLOOP
Record sputtered and lattice molecules
IF SPTMOL
   NSCXHY(NC,NH) = NSCXHY(NC,NH) + 1
ELSE
   NLCXHY(NC,NH) = NLCXHY(NC,NH) + 1
ENDIF
ENDIF
ENDLOOP

The molecule is built using a simple recursive routine which travels around the three dimensional tree structure of a molecule, where atoms are nodes of the tree and bonds are links. Each atom is only visited once.

Routine to build molecules

SUBROUTINE BONDED(BNDLST, NLIST)

Find which atom is being dealt with now
I = BNDLST(NLIST)

Add all of the atoms bound neighbours that have not been already found

Loop through all 'bound' neighbours of this atom
LOOP J

Don't want to add this atom again if it has already been found
IF NOT FOUND(J)

Increment the number of atoms within the molecule
NLIST = NLIST + 1
Add this atom to the molecule
BNDLST(NLIST) = J
Record that atom J has been allocated to a molecule
FOUND(J) = TRUE

Get this atom to add its bound neighbours
CALL BONDED(BNDLST, NLIST)

ENDIF
ENDLOOP

RETURN

Once each atom has been examined, the composition of all molecules is known. This data can then be used to calculate physical quantities, such as the mass spectrum of ejected molecules and changes to the structure of molecular crystals.
2.8 Visualisation and Animation

An increasingly useful way of illustrating results is the use of data visualisation software. Visualisation reveals features not readily apparent in the raw data produced during a simulation, e.g. the reaction sequence between an atom and a fullerene. As simulations are dynamical, computer animation can show more information than static visualisation methods, e.g. Smith and Webb [77] observed high velocity waves after making a movie of \( C_{60} \) impact on graphite. Visualisation and animation are particularly useful for communicating simulation results to others. To this end, videos have been produced for display during poster and oral presentations at conferences [77-82], and both still images and movies are incorporated into the Loughborough Molecular Dynamics Research Group World Wide Web pages [83].

Two methods of visualising data have been routinely applied to aid the understanding of simulation results presented in this thesis. In some circumstances a two dimensional view of the system (or a section of the system) can be the most informative. To show other features of the system, "three dimensional" images may be necessary. A method for automating the production of movies from the simulation results has also been developed.

To produce postscript images of either cross sections of systems or small molecules, a postscript graphics library has been used. This allows complex images to be efficiently produced from within a FORTRAN program. For other applications a full 3D image is more useful. The public domain raytracing package ‘Rayshade’ [84] has been used to produce high quality images, with typical rendering times on a workstation of around 3 minutes per 480x480 pixel image. Complex ball-and-stick images showing bonding between atoms, and space-filling representations, have been created by automation of production of input files for Rayshade. A space filling representation of the universe is obtained by putting a sphere with a radius equal to the average radius of the atom at the position of the point mass representing each atom. For small systems (e.g. atom-fullerene interactions), ball and stick images give the greatest information. The atoms are drawn as smaller spheres and bonds are drawn as cylinders between atoms, with the radius of the cylinders scaled by the cutoff function used in the potential calculation. This ensures that the animation of processes such as bond formation is achieved in a smooth fashion and that the interactions during events such as repulsion between atoms, bond breaking or bond formation are clearly illustrated in movies. An example input file is shown in figure 2.11. The colour of the spheres can be selected on the energy (potential, kinetic or total), initial
position, or type of atom involved. The most useful method of colouring atoms has been found to be colouring on the total energy of each atom. As the energy can change considerably during a simulation, colouring on a Log scale provides more information as it enables both thermal energy and high energy impacts to be visualised. The scheme generally used for carbon, silicon & hydrogen systems is as follows

**Colour each atom according to its total energy between specified values**

COL varies between 0 (low energy) and 1/3 (high energy)

If the total energy of atom \( i \) is below a pre-set minimum value

\[
\text{IF} \ \ TE(i) < \text{MINENG}
\]

Low energy

\[
\text{COL} = 0.0
\]

If the total energy of atom \( i \) is between pre-set minimum and maximum values

\[
\text{ELSE IF} \ \ TE(i) < \text{MAXENG}
\]

Use a log scale for intermediate energies

\[
\text{COL} = \frac{(1.0/3.0) \times \log(1.0+TE(i)-\text{MINENG})}{\log(1.0+\text{MAXENG}-\text{MINENG})}
\]

If the total energy of atom \( i \) is above a pre-set maximum value

\[
\text{ELSE}
\]

High energy

\[
\text{COL} = 1.0/3.0
\]

ENDIF

HUE varies from 0 (red), to 1/3 (green), to 2/3 (blue), to 1 (red)

Use a different colouring for each atom according to its type

IF \( \text{TYPE}(i) = \text{CARBON} \)

Make carbon blue (low energy) -> red (high energy)

\[
\text{HUE} = \text{COL} + 2.0/3.0
\]

ELSE IF \( \text{TYPE}(i) = \text{SILICON} \)

Make silicon green (low energy) -> red (high energy)

\[
\text{HUE} = 1.0/3.0 - \text{COL}
\]

ELSE

Make hydrogen cyan (low energy) -> orange (high energy)

\[
\text{HUE} = 1.0/2.0 - \text{COL}
\]

ENDIF

**Convert to RedGreenBlue values for Rayshade**

\[
\text{RED} = 0.41 + 0.41 \times \cos(2\pi \times \text{HUE})
\]

\[
\text{GREEN} = 0.41 + 0.41 \times \cos(2\pi \times (\text{HUE}-1.0/3.0))
\]

\[
\text{BLUE} = 0.41 + 0.41 \times \cos(2\pi \times (\text{HUE}-2.0/3.0))
\]
To create a movie, a large number of frames are rendered, stored, and then displayed in sequence to give the impression of a moving image. A typical 480x480 pixel image produced by Rayshade has a size of 90 kilobytes when stored as a GIF file. The storage requirements can be somewhat reduced by converting the files from a bitmap to JPEG (JFIF) [85] format. Using a high quality setting of 80 when converting to JPEG format leads to file sizes of around 48...
55 kilobytes. Several methods of animation have been used. For producing quick, but rough animations of less than 20 frames, the files are buffered and played back using an X-windows animation tool [86]. This is useful when examining results of simulations. Movies have been made available on the World Wide Web site by compressing a sequence of images into the MPEG [87] movie format. To transfer movies from computer to video, the Parallax Video Software and Hardware System (release 3.0.6) [88] has been used. With this system, a JPEG-movie stream is created from a series of individual JFIF files and stored on hard-disk. The Parallax system contains hardware that can uncompress this stream in real time. To play or record a movie the movie file is read for the disk, uncompressed and displayed. A typical movie contains around 1000 frames, each of about 55 kilobytes (no temporal compression is used) and so requires around 55 megabytes of storage. During the research involved with this thesis, over one gigabyte of animation has been produced. The Parallax system is only component of the visualisation process that is a commercial package. All rendering, viewing and conversion between file formats is accomplished with public domain software [84,89,85-87].

2.9 New Molecular Dynamics Program

The algorithms described in the previous sections have been incorporated into a new MD simulation program. The reasons for producing this new program are several. The existing code used at Loughborough was based on Harrison's QDYN program [1], and had been modified by several people at various times. It contained much redundant or inefficient code and could not be guaranteed to be completely robust. As several new routines and potential functions had been developed, it was easier to incorporate them into a new program than make extensive modifications to the existing code. The new program has been optimised for use in simulations of up to 100,000 atoms using many-body, short-ranged empirical potentials run on single workstations. The code is written in Fortran, using only the f77 standard and standard extensions to the language and is completely portable. So far it has been tested on SUN, IBM and HP workstations, and with the public domain g77 compiler (The Free Software Foundation's GNU project F77 Compiler) [90] where it compiles and runs on without any modification of the source. The program is currently used at Loughborough University, The University of Newcastle in Australia, and The University of Surrey.

To verify that the program is efficient, timing information was obtained from running typical simulations on several different platforms. The test
simulation involved a 250 eV \text{C}_60 incident at 60° to normal on a one monolayer hydrogen terminated \text{Si}(100)2\times1 surface. The target contained 16 layers, each of 288 silicon atoms and the one hydrogen layer, giving a total of 4956 atoms. At the start of the simulation the system was heated to 300 K and allowed to equilibrate for 100 fs. The trajectory was then run for 2.0 ps at a fixed timestep of 0.2 fs, with the silicon atoms coupled to a Berendsen bath kept at 300 K. Timing information was obtained by compiling the program with the \texttt{-pg} option to enable profiling with the UNIX \texttt{gprof} utility. The total runtime for the program on different platforms tested is given below. In all cases, several combinations of compiler options were tried to obtain the fastest executable program and only the most efficient is presented for each case in table 2.2. The results of the simulation were checked to ensure that severe optimisation did not result in erroneous execution of the code.

<table>
<thead>
<tr>
<th>Platform</th>
<th>Compiler and options</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP 9000 a</td>
<td>\texttt{if77 a} +O3</td>
<td>3220</td>
</tr>
<tr>
<td>SUN b</td>
<td>\texttt{g77 b} -O3 -ffast-math -funroll-loops -msupersparc</td>
<td>6609</td>
</tr>
<tr>
<td>SUN c</td>
<td>\texttt{g77 b} -O3 -ffast-math -funroll-loops -msupersparc</td>
<td>8530</td>
</tr>
<tr>
<td>SUN d</td>
<td>\texttt{if77 x} -fast -O4 -cg92</td>
<td>8837</td>
</tr>
<tr>
<td>SUN e</td>
<td>\texttt{if77 x} -fast -O4 -cg92</td>
<td>10108</td>
</tr>
<tr>
<td>SUN e</td>
<td>\texttt{if77 x} -fast -O4 -cg92</td>
<td>10989</td>
</tr>
<tr>
<td>IBM RS6000 e</td>
<td>\texttt{xlf} -O3 -Pk -qhsflt -qnosave -qarch=ppc</td>
<td>22836</td>
</tr>
</tbody>
</table>

Table 2.2. Performance of the program running optimised on various platforms.

a 755 125MHz PA7150 running HP-UX 9.0
b SS10 75MHz SuperSPARC II with 1Mb Cache running Solaris 2.4
c SS20 60MHz SuperSPARC with 1Mb Cache running Solaris 2.4
d SS10 75MHz SuperSPARC II with 1Mb Cache running SunOS 4.1.4
e 250 66MHz PPC 601 running AIX 3.2.5.1

All machines had at least 64Mb RAM

\(\alpha\) HP-UX fortran compiler version 73.53
\(\beta\) GNU fortran compiler version 0.5.5
\(\chi\) SUN fortran compiler version 3.0.1
\(\delta\) IBM fortran compiler version 2.3.0.35

Although the results of the simulations were all qualitatively similar (chemsorption of the fullerene in the surface silicon layers), the trajectories...
diverged from each other as the simulations ran. As the level of optimisation was increased, this divergence became more apparent due to the effects of differing hardware and the level of sophistication of the optimisation routines used in the compilers. A breakdown of the time taken in the main parts of the calculation is given below for the program compiled with g77 and running on a SUN Sparc-10 (compiler β and platform b).

<table>
<thead>
<tr>
<th>Routine</th>
<th>%Time</th>
<th>Time (s)</th>
<th>Calls</th>
<th>Time/call (s)</th>
<th>Time/call/atom (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential</td>
<td>90.6</td>
<td>5990.70</td>
<td>10508</td>
<td>0.570</td>
<td>0.115</td>
</tr>
<tr>
<td>Integration</td>
<td>2.7</td>
<td>177.89</td>
<td>1</td>
<td>177.89</td>
<td>23.78</td>
</tr>
<tr>
<td>Neighbour-list</td>
<td>2.7</td>
<td>174.18</td>
<td>542</td>
<td>0.32</td>
<td>0.065</td>
</tr>
<tr>
<td>Thermal bath</td>
<td>0.5</td>
<td>32.32</td>
<td>10502</td>
<td>0.0031</td>
<td>0.00063</td>
</tr>
<tr>
<td>Heating</td>
<td>0.2</td>
<td>11.83</td>
<td>1</td>
<td>11.83</td>
<td>2.39</td>
</tr>
</tbody>
</table>

Table 2.3. Breakdown of CPU usage during a typical simulation.

The program runs at a speed of approximately 0.127 ms per atom per timestep on this platform and runtime scales linearly with the number of atoms.
Chapter 3

Potential Functions For Covalent Materials

3.1 Introduction

The potential function is responsible for describing the 'chemistry' occurring within in a MD simulation. For energetic, or large scale (more than a few hundred atoms) simulations, the use of an approximate empirical potential is necessary as ab-initio calculations are too time consuming for any current computers. Many-body empirical potentials have been used in all the simulations described in thesis, as they can often model interactions accurately, whilst allowing systems of tens of thousands of atoms to be simulated on computer workstations.

An empirical potential may be defined as a functional that gives the total potential energy of a given system in terms of the positions of the atomic nuclei. In the Born-Oppenheimer approximation the electrons are treated as if they are always in their ground state. This implies that an energy functional exists in most cases [91]. The assumption that the positions of nuclei uniquely determines the state of electrons may be invalid for the treatment of defects within semiconductors, where multiple long-lived charge states can occur. As differing charge states lead to differing configurational energies, empirical potentials will not reliably model these defects. However the assumption is used as it is valid for most configurations and it is extremely difficult to develop an empirical potential that allows electrons to exist in multiple states.

Empirical potential functions are usually produced in two stages. First, a functional form containing free parameters is obtained. This form can be either produced by theoretical analysis, assumed based on intuition, or obtained by a combination of both approaches. For example, the functional form of Tersoff-type potentials is based on a theoretically derived pair term and a many-body term that combines theoretical models and an assumed angular term. In general, the form of angular terms contained within many-body potentials is assumed, rather than a derived by theoretic analysis. Once a functional form has been produced, values are specified for the free parameters by requiring the potential to reproduce, to within some tolerance, experimental or accurate ab-initio data. Typical data used in fitting are bond-lengths and cohesive energies of bulk structures, elastic
constants, and defect and surface energies. Assumptions made during theoretical derivation, the form of intuitively assumed components, the chosen fitting set and the fitting procedure can all affect the accuracy and transferability of the potential that is produced. No empirical potential function can be expected too give an accurate global description of a material, but configurations not too dissimilar from those fitted should be modelled with reasonable accuracy. Furthermore, if the functional form of the potential has been carefully chosen, the potential should be transferable to structures not accounted for in the fitting procedure.

Due to the enormous number of applications for silicon technology, a great deal of experimental and theoretical work has been focused on gaining understanding of the material properties of this element. The number of groups conducting molecular dynamics simulations of silicon systems is reflected in the abundance of empirical potential functions in the literature, for example see references [13,92-100]. Many of these functions have been adapted to describe other covalent elements, either by a reparameterisation or by modifications to the form of the potential. Hence there are several potentials available that model carbon or germanium systems [101-104]. The availability of individual potentials sharing the same functional form has enabled the production of multicomponent potentials for group IV systems [102-104], and potentials for III-V alloys have been produced in a similar manner [105,106]. Recently, interest in chemical vapour deposition of carbon and silicon and the effects of interstitial hydrogen in silicon has stimulated the development of potentials that describe bonding in group IV-hydrogen systems [65,107,108].

In this chapter, the potential functions that have been used are described, and a new potential that models the tri-component C/Si/H system is presented. Testing of these potential functions has shown that their transferability can be limited. If this is the case, it is sometimes necessary to modify the potential before commencing simulations.

3.2 Advances in Empirical Potential Functions

A first approximation in describing the potential energy of a system is to assume interactions can be modelled by pair terms such as the Lennard-Jones, or Morse potentials. Describing a system of condensed matter by such potentials produces close packed structures as atoms seek to achieve the maximum coordination. To model the open structures of covalent materials, an angle dependent term is required to stabilise their crystal structures. The simplest way to achieve this is to extend the expansion of the potential energy to include a three
body term. The total energy of a system where \( r_i \) are the positions of the atomic nuclei, is then written as

\[
V = \frac{1}{2} \sum_{i,j} V_2(r_i, r_j) + \frac{1}{3!} \sum_{i,j,k} V_3(r_i, r_j, r_k)
\]  

(3.2.1)

where \( V_2 \) is a pair term and \( V_3 \) includes an assumed angular term. This form was successfully used to model bulk silicon by Stillinger and Weber [92]. A drawback of the Stillinger-Weber potential is that the fitting the angular term to make the diamond structure the ground state, produced a function which is basically an expansion of the potential surface around the tetrahedral structure. The transferability of the potential to other structures is limited. The potential does not correctly model undercoordinated or overcoordinated silicon atoms [98,99] and so is not suitable for describing silicon surfaces or small clusters. An alternative approach is to abandon any expansion through third and higher order terms. A potential based on a pair function between atoms, but with a many body term that takes account of the dependence of bond energy on the local environment, gives the possibility of greater accuracy and transferability. A general \( n \)-body potential expression is given by

\[
V = \frac{1}{2} \sum_{i,j} V_2(r_i, r_j) + \sum_i U \left( \sum_j g_2(r_i, r_j), \sum_{j,k} g_3(r_i, r_j, r_k) \right)...
\]  

(3.2.2)

where \( V_2 \) is a pair term and \( U \) is a many-body term dependent on the local environment. One of the most successful of these cluster functionals is the Tersoff formalism [13], in which the many-body term includes two and three body functions.

The majority of potential functions for semiconductors have been developed for simulations involving properties of bulk material. It is not surprising that these empirical potentials are inaccurate when applied to the study of clusters and do not reproduce all the subtle chemistry that causes the reconstruction of surfaces. For instance, both S-W and Tersoff silicon potentials are qualitatively correct in predicting the dimer reconstruction on the \( Si(100) \) to be energetically preferred, although the energy gain on dimerisation is not always given to a great accuracy. Both potentials predict a symmetric dimer, whereas experiment and \textit{ab-initio} calculation have shown that the lowest energy structure consists of buckled dimers, although the predicted energy gain with symmetry breaking is small [109]. The Tersoff potentials correctly predict a dimer length
less than the bulk bond length, while the S-W potential predicts the dimer length to be greater than the bulk bond length. More subtle changes such as the 7x7 reconstruction that occur on the Si{111} surface are less accurately described. The S-W potential predicts the unrelaxed bulk surface to be the most stable, whereas the predictions of the Tersoff potentials differ depending upon the parameterisation being used. The dimer reconstruction is driven by the need to reduce the number of dangling bonds on the surface, and so is described at least qualitatively by most silicon potentials [99]. The 7x7 reconstruction involves dimerisation, and the production of adatoms and stacking faults (the DAS model [110,111]). Its stability is due to the reduction of the number dangling bonds, at the expense of an increase in strained bond angles, and so empirical predictions are sensitive to the angular term used in the potential. As the form of the angular term is assumed, and usually fitted to bulk silicon, it is not surprising that inaccuracies arise. The necessity for computational efficiency of these potentials also causes long range effects such as torsion and π bonding to be ignored, leading to inaccuracies in the description of clusters. For these reasons, care must be taken to determine the accuracy of a given potential for each application. As long as the accuracy of the empirical potential has been verified, classical simulations can give great insights into the behaviour of covalent materials.

The rapidly increasing processing power available from modern computers enables the implementation of more accurate potential functions. Recent advancements with methods such as the bond order potential [25,112-114] have led to the possibility of conducting simulations involving some degree of quantum calculation. The motivation behind the potential is that bond formation is a quantum mechanical effect and so cannot be properly described by an empirical model, hence some electronic detail must be included within the calculation. The bond order potential is based on the Lanczos tight binding recursion method (LTBRM). A generalised many-body expansion of the intersite (IS) Green’s functions is used to give good convergence of the bond energy and ensure equivalence between the IS and site diagonal (SD) approaches. The time taken for the potential and force calculation scales linearly with the number of atoms, with typical figures for a workstation (IBM RS6000/550) being around 30 seconds per timestep for a 100 atom system [25,113]. This is around 2000 times slower than calculations conducted on a similar machine using a many-body empirical potential, e.g. see section 2.9. The method is still too computational expensive to routinely conduct large scale simulations, but is more accurate then empirical potentials and faster than full ab-initio calculations such as Car-Parrinello [23] molecular dynamics. Hence, for certain types of calculation, the bond order potential should be more useful than either empirical or ab-initio methods.
Recently it was shown that the expression given by the bond order potential for the angular term for silicon is equivalent to that used in the Tersoff potential [114]. As well as validating the Tersoff potential, this suggests that by using the tight binding potential, it may be possible to extract other functional forms. If this were possible, it would allow the parameterisation of an empirical potential containing higher order functionals. Such a potential would be expected to be more accurate and/or more transferable than existing potentials.

3.3 The Tersoff Potential Formalism

3.3.1 Outline of the Potential

The form of the potential was motivated by theoretical results relating bond order to the local atomic environment. As the coordination of an atom increases, the strength of each bond it forms is decreased. The dependence of bond energy on coordination is explicitly included in the formalism of the potential, where the energy of a bond is modelled by a repulsive pair term and an attractive term that is modified by a many body function dependent upon the local environment. As the potential is explicitly based on the bond order of atoms, it should be more transferable to structures not included in the fitting set than potentials based on a general expansion of the potential energy.

The potential uses ideas developed by Pauling [115], Ferrante, Smith & Rose (hereafter referred to as FSR) [116,117], and Abell [118]. FSR discovered a single relation between binding energy and interatomic spacing that described the energetics of diatomic molecules, bulk metals, metal interfaces, and gas atom-metal interactions. By choosing appropriate energy and length scaling factors, curves of binding energy as a function of interaction distance obtained by ab-initio calculations for typical interactions were all mapped onto the same universal function. The total energy $E$, can be written as a function of the interatomic separation $r$, using the universal relation $E^*$, by

$$E(a) = \Delta E \cdot E^*(r^*) \text{ where } r^* = (r - r_e)/l$$

(3.3.1)

where $\Delta E$ and $r_e$ are the equilibrium binding energy and atomic separation, respectively, and $l$ is the scaling length. The shape of the universal function $E^*$ is similar to that of the Morse potential. Abell analysed molecular and metallic binding, using chemical pseudopotential theory. He produced an expression for the binding energy in terms of bond densities and pair interactions. Assuming that
the pair interactions can be expressed as exponentials. The binding energy per atom for a given interaction topology is given by

$$\varepsilon_b(r) = Z\left[A_q \exp(-\lambda r) - B_p G_q \exp(-\mu r)\right]$$  \hspace{1cm} (3.3.2)$$

where \( r \) is the interatomic distance, \( Z \) is the number of nearest-neighbour atoms, \( q \) is the number of valence electrons per atom and \( p \) is the bond order. The local interaction topology is represented by \( G \), and \( A, B, \lambda \) and \( \mu \) are parameters of the exponential functions that are characteristic of a given atomic species. The relationship between bond length and bond order that the analysis produced is identical in form to the empirical expression produced by Pauling. For a given atomic structure, the expression for the binding energy can be scaled to a function with only one free parameter by applying the same scaling procedure as FSR. The binding energy can be written as

$$\varepsilon_b(r) = D_v \varepsilon'_b(r^*)$$

where

$$\varepsilon'_b(r^*) = \left[\exp\left(-S^2 r^*\right) - S \exp\left(-S^{-2} r^*\right)\right]/(S - 1)$$

and

$$S = \lambda/\mu, \quad r^* = (r - r_e)(\lambda/\mu)^{1/2}$$

$$r_e = (\lambda - \mu)^{-1} \ln(ASq/Bp), \quad D_v = Zaq(S - 1)\exp(-\lambda r_e)$$  \hspace{1cm} (3.3.3)$$

where \( S \) is the only remaining parameter in the scaled energy function. Abell showed that the scaled energy function was consistent with the observations of FSR for reasonable choices of this parameter, i.e. \( S \) has little affect on the shape of the scaled binding energy curve. However, structural preference of a given atomic species depended exponentially on this parameter.

Tersoff’s potential is based on equations (3.3.2) and (3.3.3), but includes an explicit expression for the bond order term \( p \). The potential described below is an improvement on an earlier potential \cite{119} with a different functional form for the bond order term. Although this earlier potential was promising, it did not give diamond lattice structure as the ground state for silicon. The Tersoff and related potentials are descended from the potential described in reference \cite{13} and outlined below.

The total potential energy is written as a sum over pairs

$$V = \frac{1}{2} \sum_{i \neq j} \Phi_{ij}$$  \hspace{1cm} (3.3.4)$$

57
\[ \Phi_{ij} = f(r_{ij}) \left[ V_h(r_{ij}) - b_{ij} V_A(r_{ij}) \right] \]  

(3.3.5)

where \( V_h(r_{ij}) \) and \( V_A(r_{ij}) \) are pair terms, \( r_{ij} \) is the length of the bond between atoms \( i \) and \( j \), and \( b_{ij} \) is a many-body function that can be regarded as an effective Pauling bond order \[115\]. The bond order term is centred on one atom, so for the bond \( i-j \), \( b_{ij} \neq b_{ji} \). The cutoff function, that restricts the potential to nearest neighbours is given by

\[ f(r_{ij}) = \begin{cases} 
1, & r_{ij} \leq R^{(1)} \\
1 + \cos \left( \frac{\pi (r_{ij} - R^{(1)})}{(R^{(2)} - R^{(1)})} \right), & R^{(1)} < r_{ij} < R^{(2)} \\
0, & r_{ij} \geq R^{(2)} 
\end{cases} \]  

(3.3.6)

This ensures that all interactions decay smoothly to zero between separations of \( R^{(1)} \) and \( R^{(2)} \). \( V_h(r_{ij}) \) and \( V_A(r_{ij}) \) are the repulsive and attractive components respectively of a Morse-type potential.

\[ V_h(r_{ij}) = A \exp(-\lambda r_{ij}) \]  

(3.3.7)

\[ V_A(r_{ij}) = B \exp(-\mu r_{ij}) \]  

(3.3.8)

The repulsive term is pairwise, whilst the attractive term is modified by a many-body function introduced by Tersoff to account for the local environment of atom \( i \). The bond order expression for atom \( i \) is

\[ b_{ij} = \left[ 1 + \zeta_{ij} \right]^{\delta} \]  

(3.3.9)

with competition between bonds described by

\[ \zeta_{ij} = \sum_{k \neq i, j} f(r_{ik}) g(\theta_{ik}) \exp \left[ \alpha (r_{ij} - r_{ik})^\beta \right] \]  

(3.3.10)

The exponential term models the weakening of long bonds due to the presence of shorter bonds on the same atom, whilst the angular term describes strain due to bond angles differing from some optimum angle. The length dependent term in the calculation of \( \zeta_{ij} \) is sometimes omitted, as this greatly simplifies the form of
the potential without having a significant effect on its performance. The usual form for the term in bond angles is

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

(3.3.11)

where \( \theta \) is the angle formed between the bond from \( i \) to \( j \) and another bond on atom \( i \). The parameter \( h \) is the cosine of the optimum bond angle and the parameters \( a, c \) and \( d \) control the size and relative importance of contributions due to coordination and bond angles.

Using this functional form, the equilibrium bond length for a given value for the bond order term \( b_{ij} \), is given by

\[ r = (\lambda - \mu)^{-1} \ln \left( \frac{1}{b_{ij}} \right) \left( \frac{\lambda A}{\mu B} \right) \]  

(3.3.12)

which is equivalent to the relationship between bond order and bond length derived theoretically by Abell and empirically by Pauling. Similarly, the energy of one bond (assuming a symmetric structure where \( b_{ij} = b_{ji} \)) is given by

\[ \Phi_{ij} = (\lambda - \mu) \left[ \left( \frac{\mu}{A} \right)^{\mu} \left( \frac{b_{ij} B^{-\lambda}}{\lambda} \right)^{1/(\lambda - \mu)} \right] \]

i.e.

\[ \Phi_{ij} \propto (b_{ij})^{S(s-1)}, \text{ where } S = \lambda/\mu \]

(3.3.13)

which is the same as that produced by Abell.

3.3.2 Similarity Between Tersoff Potentials and the Embedded-Atom Method

Tersoff's potentials were developed to describe condensed phases of covalent materials and at first glance appear to be distinct from all other formalisms. Daw & Baskes [10,11] developed the embedded-atom method (EAM) to describe the interatomic forces in metals several years prior to the development of the Tersoff-Abell potential expression. Brenner has shown for a reasonable choice of functional forms and parameters, that these two expressions are very similar [120].
For both functions, the total potential energy is written as a sum over atomic sites, with the energy of each atom being written as a pair sum plus a many-body function. If cutoff functions are neglected, this can be written as

\[ V = \sum_i V_i \quad V_i = \frac{1}{2} \sum_{j \neq i} V_i^p(r_{ij}) + V_i^{mb} \]  

(3.3.14)

The pair sum can be regarded as screened core-core repulsion between individual pairs of atoms, whilst the many-body term is due to bonding and is attractive.

Using the most general form for the bond order term, the attractive part of the Tersoff potential can be written as

\[ V_i^{mb} = -\frac{1}{2} \sum_{j \neq i} B e^{-\alpha r_{ij}} \left[ 1 + \left\{ \sum_{k \neq i,j} \delta \left( \theta_{jk} \right) e^{\alpha (r_{ij} - r_{kj})} \right\}^{\eta} \right]^\delta \]  

(3.3.15)

Using the Finnis-Sinclair [12] expression for the embedding function and assuming an exponential form for the atomic electron density [121], the many-body term in the EAM formalism is

\[ V_i^{mb} = -C \left[ \sum_{j \neq i} e^{-\alpha r_{ij}} \right]^{-\frac{1}{2}} \]  

(3.3.16)

This can be rewritten in the following manner

\[ V_i^{mb} = -C \left[ \sum_{j \neq i} e^{-\alpha r_{ij}} \right] \left[ \sum_{k \neq i} e^{-\alpha r_{ik}} \right]^{-1/2} \]

\[ = -C \sum_{j \neq i} \left[ e^{-\alpha r_{ij}} \left[ e^{-\alpha r_{ij}} + \sum_{k \neq i,j} e^{-\alpha r_{ik}} \right]^{-1/2} \right] \]

(3.3.17)

\[ = -\sum_{j \neq i} \left[ Ce^{-\alpha r_{ij}} \left[ e^{-\alpha r_{ij}} + \sum_{k \neq i,j} e^{-\alpha r_{ik}} \right]^{-1/2} \right] \]

\[ = -\sum_{j \neq i} \left[ Ce^{-\alpha r_{ij}} \left[ 1 + \sum_{k \neq i,j} e^{\alpha (r_{ij} - r_{kj})} \right]^{-1/2} \right] \]
If \( B = 2C, \alpha = a = 2\mu, \beta = 1, \eta = 1, \delta = -\frac{1}{2} \) and \( g(\theta_{ij}) \) is taken to be unity in equation (3.3.15), then the expressions for the two forms become identical. This emphasises the similarities in the potentials and also highlights the main difference between the two. The explicit inclusion of angular terms in the Tersoff potential is necessary due to the more open structures associated with covalent bonding. An attempt to produce an EAM potential for silicon [95] required such an angle dependent term to be added to the many-body part of the expression. Garrison and co-workers [122,21] have also constructed hybrid potentials incorporating both Tersoff and EAM functions to model metal-hydrocarbon systems.

### 3.3.3 Deficiencies of the Tersoff Formalism

In many cases, Tersoff's potential can be reasonably applied to model structures not accounted for in the fitting procedure. There are however, certain situations where the functional form and short range of the potential causes it to break down. The potential is unable to give a proper description of bonding in radicals or to differentiate between conjugated and non-conjugated systems in carbon [65].

For example, consider the energy calculation for bond \( i-j \) in the case illustrated below.

**Figure 3.1. An example of an overbinding of radicals predicted by Tersoff's potential.**

The bond-order term for atom \( i \) will treat this bond as a single bond, whilst the bond-order term for \( j \) will treat the bond as if it has some double bond character. Hence the calculated bond will be intermediate between a single and double bond. However this bond cannot have any double bond character as atom \( i \) has no free orbitals. The bond is better described as a single bond plus the radical orbital due to atom \( j \), giving a different length and energy. This deficiency in the potential results in a non-physical description of a number of common situations. The formation of a vacancy in the diamond structure will produce four radicals of the kind described above. This explains the difficulty of fitting the energy of
vacancies which lead to threefold coordinated atoms whilst at the same time
describing bulk structures such as graphite which are also threefold coordinated.
To correct for this deficiency, the bond order term must be modified when atoms $i$
and $j$ have differing numbers of neighbours.

The failure of the potential to describe both conjugated and non-
conjugated systems is illustrated by the following example.

![Figure 3.2. An example of the failure by Tersoff's potential to account for
conjugation.](image)

In both situations, the atoms involved in the bond have the same local
environment, so the bonds are treated in an identical fashion. Where neighbours
have a coordination of three, e.g. in graphite, the bond is part of a conjugated
system and has approximately one-third double bond and two-thirds single bond
character. If all neighbours have a coordination of four, the system is not
conjugated and the bond has complete double bond character. These bonds
therefore should have differing energies and lengths. There is no way to allow for
this without including non-local effects into the potential.

Brenner has proposed a method of correcting both these shortcomings of
the potential by the addition of an extra function to the bond-order term of the
potential. No functional form could be found that fitted the data, so the function is
expressed as a ‘spline’ through data points. This is detailed in the description of
the hydrocarbon potential in section 3.4.4.

Another problem with the potential is that the repulsive term is fit to
describe the equilibrium energy, geometry and elastic properties of bulk
polytypes. The function is not sufficiently repulsive for close range interactions,
which are more accurately modelled by a screened Coulomb potential, such as the
Molière potential [123]. To overcome this deficiency, the Tersoff repulsive term
can be smoothly joined to a screened coulomb function for close interactions. The
method chosen in this thesis to accomplish the fitting is that proposed by Smith,
Harrison and Garrison [69], and is described in section 3.6.
3.4 Potentials Based on the Tersoff Formalism

3.4.1 Introduction

Tersoff's original potential [13] was parameterised to describe the bulk and surface properties of silicon. The potential has been refit to describe other group IV elements, and to improve the modelling of elastic properties of silicon [97,101-103]. As the same functional form can describe different elements, depending upon the parameterisation, the potential can be extended to multi-component systems. This has been shown to be a straightforward procedure, by using an interpolation scheme to generate parameters for mixed bonds. A similar approach has also been used to develop potentials for III-V alloys such as gallium/arsenic and aluminium/arsenic [106,70], whilst attempts are currently being made to develop a similar potential for boron/nitrogen systems [124]. Brenner has shown [125] that Tersoff-type potentials may be applied to chemical systems other than those of covalent materials. He produced potentials to describe a gas-phase few-body reactive system ($H_3$), and a molecular solid (oxygen). The ability of the potential formalism to describe bonding between hydrogen atoms in addition to bonding in group-IV elements has led to the production of hydrogen/group-IV potentials. These potentials are necessary for the simulation of diamond growth by CVD, and silicon processing techniques.

3.4.2 Potentials for Single Element Systems

Tersoff has produced two parameterisations [13,97] of his potential function to describe silicon systems. The original parameterisation was fit to a database consisting of the cohesive energy, lattice constant, and bulk modulus of diamond silicon, and the calculated cohesive energy of the hypothetical graphitic and simple cubic phases. This potential gave a good overall description of the properties of silicon, except for a very poor description of bond-bending forces. A second parameterisation was specified, fit to the same database, but with the added constraint that all three elastic constants of silicon should be specified to within 20%. This second parameterisation accurately reproduces the elastic constants, but at the expense of a reduction in the accuracy of the description of highly rebonded surfaces. The energy gain associated with dimerisation of the $Si\{100\}$ surface is 2.4 eV per dimer with the first parameterisation and 1.4 eV with the second, compared to a value of 2 eV from LDA calculations [97]. Results are less accurate for reconstruction of the $\{111\}$ surface. The first
parameterisation predicts the top and hollow threefold sites to be energetically preferable to the relaxed $1\times1$ surface, but the second incorrectly predicts that adatoms on the $\{111\}$ surface raise the energy rather than lower it.

Tersoff has also produced two parameterisations for carbon [101,103]. The first parameterisation was fit to a database consisting of the cohesive energy of carbon polytypes and the lattice constant and bulk modulus of diamond, with the additional constraint that the vacancy in diamond had a formation energy of at least 4 eV. This potential describes the cohesive energy of carbon well, for both graphite and diamond phases. Elastic constants are also described satisfactorily, though the accuracy is less for graphite, this is to be expected due to the fitting procedure. The second parameterisation was fit to the same database, but made to reproduce the vacancy energy in diamond of 7 eV. A side effect of this tighter constraint is to further reduce the accuracy of the description of graphite due to the reasons detailed in section 3.3.3.

There is also a parameterisation that describes germanium systems [102], again fitted to available polytype energies. In addition, Brenner has produced two parameterisations of an alternative carbon potential [126,65].

### 3.4.3 Potentials for Multicomponent Group IV Systems

Tersoff has shown that it is straightforward to combine the potentials for single element systems to produce a potential for a two-component system [103]. The approach is to use parameters first fit to single element systems. Parameters for heteronuclear bonds are generated by interpolation between the values for the respective single element systems. One additional parameter is introduced to modify the attractive term in each heteropolar bond; this is fit to reproduce the heat of formation of the zinc-blende structure compound. The single set of parameters used in the one element case is replaced by three sets of bond centred parameters for the pair terms and two sets of atom centred parameters for the bond order term.

Rewriting equations (3.3.1-8) to explicitly show the dependence of the parameters on element types gives

\[
V = \frac{1}{2} \sum_{i\neq j} \Phi_{ij} \quad (3.4.1)
\]

\[
\Phi_{ij} = f_{ij}(r_{ij})[V_B(r_{ij}) - b_{ij}V_A(r_{ij})] \quad (3.4.2)
\]
To simplify the potential, length dependent terms in the calculation of $r_{ij}$ are omitted.

Parameters for single element bonds and for the bond order terms are those used in the single-component potentials discussed above. The additional parameters for heteronuclear bonds are obtained via the following interpolation scheme,

$$R_{ij} = \left[ 1 + \frac{\pi (r_{ij} - R_{ij}^{(1)})}{(R_{ij}^{(2)} - R_{ij}^{(1)})} \right]^{1/2}$$

where $x_{ij}$ is the additional parameter fitted to the heat of formation of the zinc-blende compound.

Potentials for silicon-carbon and silicon-germanium systems have been developed in this fashion.
3.4.4 Brenner's Hydrocarbon Potential

This potential was developed in order to enable large-scale simulations of the chemical vapour deposition (CVD) of diamond films. The potential is based on Tersoff's formalism, but includes extra terms to overcome some deficiencies of the original potential and to account for non-local effects. The full parameterisation of the potential is given in section 3.4.6.

The binding energy is rewritten as

$$V = \sum_{i<j} f_{ij}(r_{ij})\left[V_B(r_{ij}) - \bar{b}_{ij} V_A(r_{ij})\right]$$

(3.4.10)

and the bond order term is given by

$$\bar{b}_{ij} = \left[ b_{ij} + F_{cc} \left(N_{ij}^{\alpha}, N_{ij}^{\beta}, N_{ij}^{\text{conq}}\right) \right]/2$$

(3.4.11)

where $F_{cc}$ is applied to carbon-carbon bonds only. $F_{cc}$ is a term to correct for the overbinding of radicals and also includes non-local effects to model conjugation. An additional term of the form

$$C_{cc} \left(N_{ij}^{\alpha}, N_{ij}^{\beta}, N_{ij}^{\text{conq}}\right) T_{ij}^{\text{dihedral}}$$

(3.4.12)

may also be added to $\bar{b}_{ij}$ for carbon-carbon bonds [126]. This is a four-body term that is added to $\bar{b}_{ij}$ if the simulation requires a good description of torsional forces. $T_{ij}^{\text{dihedral}}$ is a penalty function for the bond $ij$ that penalises non-planar molecules. It is given by

$$T_{ij}^{\text{dihedral}} = \sum_{k, l, i, j, k} \left[ 1 - \cos^2 \omega_{ijkl} \right] f_{kl}(r_{ik}) f_{lj}(r_{jk})$$

(3.4.13)

where $\omega_{ijkl}$ is the dihedral angle for neighbours $k$ and $l$ of $i$ and $j$ respectively. The angular term is given by

$$\cos \omega_{ijkl} = \mathbf{e}_{ik} \cdot \mathbf{e}_{lj}$$

(3.4.14)

where $\mathbf{e}_{ik}$ and $\mathbf{e}_{lj}$ are unit vectors in the directions of the cross products $\mathbf{r}_{ij} \times \mathbf{r}_{ik}$ and $\mathbf{r}_{ij} \times \mathbf{r}_{lj}$ respectively.
The contribution from atom \(i\) to the bond order term is

\[
b_{ij} = \left[ 1 + \zeta_{ji} + H_{ij} \left( N_{ij}^{(C)}, N_{ij}^{(H)} \right) \right]^{-\delta_{ij}}
\]  
(3.4.15)

where \(H_{ij}\) is a function to account for the large difference in bonding characteristics between carbon and hydrogen, and is applied for all carbon atoms. The functions \(F_{CC}, C_{CC}, H_{CC}\), and \(H_{CH}\) are obtained by interpolation between data fit to integer values of coordination and conjugation. Although Brenner refers to the interpolation functions as cubic splines, the method used for their evaluation is in fact cubic interpolation [127], i.e. the cubic polynomials are fit to function values and derivatives, rather than only fitting function values and specifying first derivatives to ensure continuity of the second derivative.

The quantities \(N_{ij}^{(C)}\) and \(N_{ij}^{(H)}\) are evaluated for all carbon atoms and are the number of carbon and hydrogen atoms, respectively, that are bonded to atom \(i\), excluding atom \(j\). These definitions differ from the published version of the potential, which does not state that atom \(j\) is excluded from the coordination counts. The exclusion is implied by the data used in fitting the spline functions and has been confirmed by Brenner [127]. To make the quantities continuous, the cutoff function is used to define connectivity

\[
N_{ij}^{(C)} = \sum_{k \neq j} f_{ik}(r_{ik}) \\
N_{ij}^{(H)} = \sum_{k \neq j} f_{ik}(r_{ik})
\]

(3.4.16)

\(N_{ij}^{(C)}\) is the total number of neighbours of atom \(i\), excluding atom \(j\).

\[
N_{ij}^{(H)} = N_{ij}^{(C)} + N_{ij}^{(H)}
\]

(3.4.17)

A bond is defined as being part of a conjugated system if any neighbours of \(i\) or \(j\) have a coordination of less than 4. This is modelled by \(N_{ij}^{\text{conj}}\), where

\[
N_{ij}^{\text{conj}} = 1 + \sum_{\text{carbons } k \neq \{i,j\}} f_{ik}(r_{ik}) F(N_{ik}^{(i)}) + \sum_{\text{carbons } l \neq \{i,j\}} f_{il}(r_{il}) F(N_{il}^{(i)})
\]

(3.4.18)

and

\[
F(N_{ik}^{(i)}) = \begin{cases} 
1, & N_{ik}^{(i)} \leq 2 \\
\left[ 1 + \cos \left( \pi \left( N_{ik}^{(i)} - 2 \right) \right) \right] / 2, & 2 < N_{ik}^{(i)} < 3 \\
0, & N_{ik}^{(i)} \geq 3
\end{cases}
\]

(3.4.19)
A value of 1 for $N_{ij}^{\text{con}}$ means that the bond is not part of a conjugated system, whilst the bond is treated as being part of a conjugated system if $N_{ij}^{\text{con}}$ has a value of 2 or more.

Competition between bonds is described by

$$
\zeta_{ij} = \sum_{k \neq i,j} f_{ik}(r_{ik}) g_i(\theta_{ijk}) \exp\left[\alpha\left\{(r_{ij} - R_{ij}^{(c)}) - (r_{ik} - R_{ik}^{(c)})\right\}\right]
$$

(3.4.20)

where $R_{ij}^{(c)}$ is the equilibrium bond length for atoms $i$ and $j$. The exponential term in bond lengths is only applied where both of the bonds contain hydrogen atoms. The angle dependent term has the usual form for carbon centres, but is set to a constant value for hydrogen centres to model the fact that hydrogen is monovalent.

$$
g_c(\theta) = a\left[1 + c^2/d^3 - c^2\left[1 + (\cos \theta)^2\right]\right] \quad g_h(\theta) = a
$$

(3.4.21)

Brenner has produced two parameterisations of this potential. In the first parameterisation, the carbon component of the potential is fit to the lattice constants and binding energies of diamond and graphite, the binding energies for $C_2$, hypothetical simple-cubic and hypothetical face-centred-cubic lattices, and the barrier for conversion from rhombohedral graphite to diamond. The second carbon parameterisation was fit to the lattice constants and binding energies of diamond, graphite, hypothetical simple-cubic and hypothetical face-centred-cubic lattices. The hydrogen component is fit to the diatomic molecule and the barrier in the linear exchange reaction $H + H_2 \rightarrow H_2 + H$. The $C-H$ Morse terms are fit to the $CH$ diatomic molecule. The spline terms are then fit to the vacancy formation energies for diamond and graphite, and bond energies in various hydrocarbon molecules.

Two parameterisations of the potential were produced as no single parameterisation of the pair terms could be found that correctly reproduced the stretching force constants and lengths for carbon bonds. The first parameterisation gives single, double and triple bond lengths to within 0.02 Å, but stretching force constants differ from experimental values by as much as 60%. The second parameterisation gives the force constants to within 26%, but double and triple bond lengths are larger than the experimental values by 3.7% and 7.5%, respectively.

Both parameterisations of the potential correctly describe the energetics of diamond, graphite, vacancies in diamond and graphite, and reconstruction at
diamond surfaces. Due to the inclusion of the spline correction terms, the atomisation energies of small hydrocarbon radicals are given to a good accuracy. Calculated atomisation energies of a test set of 46 alkane, alkene, alkyne, aromatic and radical molecules agree with experimentally determined values to within 1% for 38 of the molecules. The largest discrepancies are for molecules such as $H_2CH=C=CH_2$, where the analytical approximation defining conjugation breaks down; in these cases the atomisation energy of the molecule is underestimated by approximately 0.8 eV per double bond.
3.4.5 Murty and Atwater’s Silicon-Hydrogen Potential

This potential [108] was developed to facilitate simulation of the interaction of gas-phase hydrosilicon molecules with hydrogen terminated silicon surfaces and hydrogenated amorphous silicon. These interactions are important in several device processing steps in the semiconductor industry, such as CVD growth of silicon and ion bombardment of hydrogenated silicon surfaces. The potential incorporates Tersoff’s silicon potential [97] and the hydrogen component of from the first parameterisation of Brenner’s hydrocarbon potential [65]. New parameters are introduced for the Morse term for Si-H bonds and for bond angle terms involving mixed silicon-hydrogen triples. Spline functions are incorporated into the potential to increase the accuracy of the description of Si-H bonds, and to model the dependence of the optimum silicon bond angle on coordination. A new form of the bond-angle term is introduced to allow the correct modelling of bond-centred hydrogen interstitials.

The total potential energy is written as a sum over pairs

\[
V = \frac{1}{2} \sum_{i<j} \Phi_{ij} \tag{3.4.22}
\]

\[
\Phi_{ij} = f_{ij}(r_{ij}) \left[ V_h(r_{ij}) - b_h V_s(r_{ij}) \right] \tag{3.4.23}
\]

Murty and Atwater propose a modification of the cutoff function that has two sinusoidal terms, and is given by

\[
f_{ij}(r_{ij}) = \begin{cases} 
1, & r_{ij} \leq R^{(1)}_y \\
\frac{1}{2} - \frac{2}{\pi} \sin \left[ \frac{\pi(r_{ij} - \overline{R}_y)}{(R^{(2)}_y - R^{(1)}_y)} \right] - \frac{3}{16} \sin \left[ \frac{3\pi(r_{ij} - \overline{R}_y)}{(R^{(2)}_y - R^{(1)}_y)} \right], & R^{(1)}_y < r_{ij} < R^{(2)}_y \\
0, & r_{ij} \geq R^{(2)}_y \end{cases}
\]

where \( \overline{R}_y = \frac{(R^{(1)}_y + R^{(2)}_y)}{2} \)

They argue that because this function possesses a continuous third derivative at \( R^{(1)}_y \) and \( R^{(2)}_y \), the potential should conserve energy and momentum better than when using the usual cutoff. The usual form of the cutoff function in Tersoff-type potentials is
This function has a continuous first derivative, but higher derivatives are not continuous at $R_{ij}^{(1)}$ and $R_{ij}^{(2)}$. The two forms of the cutoff function are compared in figure 3.3.

![Comparison between the usual and proposed cutoff functions of class $C^1$ and $C^3$ respectively. The cutoff limits are normalised, so $R^{(1)}=0$ and $R^{(2)}=1$.](image)

The class $C^3$ function is smoother at the end points of the cutoff region, but this leads to a steeper slope of the function at the centre of the region. The change in value of the class $C^1$ function is fairly uniform across the whole of the cutoff region. A problem with all short ranged potentials is that some form of cutoff is necessary to remove interactions beyond a specified distance. The values for the cutoff limits in Tersoff-type potentials are chosen to restrict interactions in bulk...
materials to nearest neighbours only. This results in a somewhat arbitrary and very abrupt cutoff region. The objective should be to make the cutoff as flat as possible whilst keeping the first derivative continuous. The class $C^1$ function achieves this and has been successfully applied to many potentials without any problems. Murty and Atwater argue that the continuity of the third derivative will improve the energy conservation of the potential, but the increased slope will cause the potential between two atoms to change very rapidly as their separation passes through the cutoff region. This will require a smaller timestep to maintain the accuracy of the simulation. As explained in section 2.4.1, a consequence of using a $C^3$ function is that it may be possible to use a higher order integrator than if a $C^1$ function were used, but Murty and Atwater do not mention any specific integrator for use with their potential. For implementations of the silicon-hydrogen potential presented here, the original form of the cutoff function has been used. This has no effect on any structures or atomisation energies predicted by the potential, except a very small change in the description of the dihydride $Si\{100\}$ surface. Repulsion between hydrogen atoms on this surface leads to a canted-row structure, in qualitative agreement with ab-initio calculations. This symmetry breaking displacement is driven by repulsion between hydrogen atoms, with the separation between atoms being near the extreme of the cutoff region. The use of the original cutoff function slightly increases the amount of displacement and the energy gain on forming the canted row structure, improving the agreement with results of ab-initio calculation.

$V_R(r_{ij})$ and $V_A(r_{ij})$ are the repulsive and attractive components respectively, of a modified Morse-type potential.

$$V_R(r_{ij}) = A_1 F_1 (N_{Si}^{i(i)}) \exp(-\lambda_{ij} r_{ij})$$  \hspace{1cm} (3.4.26)

$$V_A(r_{ij}) = B_1 F_2 (N_{Si}^{i(i)}) \exp(-\mu_{ij} r_{ij})$$  \hspace{1cm} (3.4.27)

The functions $F_1$ and $F_2$ are dependent upon the coordination of silicon atoms and are only used in the description of $Si-H$ bonds. To obtain a continuous function for the coordination of the $Si$ atom, it is written as

$$N_{Si}^{i(i)} = \sum f_{ij}^i (r_{ij})$$  \hspace{1cm} (3.4.28)

This differs from the coordination count used in the Brenner potential, as all atoms within the cutoff distance are counted, i.e. atom $j$ is not ignored when calculating bond $i-j$. The functions are given by cubic splines, fit to integer values
of coordination from 1 through 4, with zero derivatives at the end points. As the interpolation functions are one-dimensional, cubic splines can be used efficiently instead of the cubic interpolation used for the two and three dimensional interpolation functions in the Brenner potential. Hence the function has a continuous second derivative everywhere except at coordination values of one and four.

The contribution from atom \( i \) to the bond order term is

\[
 b_{ij} = \left[1 + \xi_{ij} \right] \delta_{ij} \tag{3.4.29}
\]

with competition between bonds described by

\[
 \xi_{ij} = \sum_{k \neq i,j} f_{ij}(r_{ik}) g_{ij}(\theta_{ijk}) \exp \left[ \alpha \left\{ (r_{ij} - R_{ij}^0) - (r_{ik} - R_{ik}^0) \right\}^2 \right] \tag{3.4.30}
\]

Depending upon the types of atoms \( i, j \) and \( k \), one of several parameterisations is used for the exponential term that deals with bond lengths. The angle dependent term is given by the function

\[
 g_{ij}(\theta) = c + d \{ h - \cos \theta \}^2 \tag{3.4.31}
\]

Two parameterisations of the function are used for \( i = \)hydrogen. One corresponds to the usual case of monovalent hydrogen and is taken from Brenner’s potential, while the other allows for bond-centred hydrogen. For \( i = \)silicon, two parameterisations are also used. One is the usual Tersoff function, and is used if \( j \) and \( k \) are both silicon. If either \( j \) or \( k \) is hydrogen, a parameterisation with \( h \) replaced by the function \( H(N_{si}^{(i)}) \) is used. \( H(N_{si}^{(i)}) \) is given by a cubic spline, fit to integer values of coordination from 1 through 4, with zero derivatives at the end points. Note that the angle dependent term for \( i = \)silicon in the Tersoff potential is used in a modified form. Tersoff [13] writes this term as

\[
 g_{si}(\theta) = a_0 \left[ 1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2} \left[ \frac{c_0^2}{d_0^2} + (h - \cos \theta)^2 \right] \right] \tag{3.4.32}
\]

which can be rearranged to give

\[
 g_{si}(\theta) = a_0 \left\{ \frac{(1 + c_0^2/d_0^2) + (1 + c_0^2/d_0^2)(h - \cos \theta)^2/d_0^2 - c_0^2/d_0^2}{1 + (h - \cos \theta)^2/d_0^2} \right\} \tag{3.4.33}
\]
In the parameterisation used, $c_0^2 >> d_0^2$, $c_0^3/d_0^4 >> 1$, $d_0^2 >> 1$ and $a_0 << 1$, so this can be approximated by

$$g_{3\theta}(\theta) = (a_0 c_0^2/d_0^4)(h - \cos \theta)^2$$  \hspace{1cm} (3.4.34)

which is the form used in the potential. The similarity of the two functions for $g_{3\theta}(\theta)$ is illustrated in figure 3.4.

![Graph showing comparison between modified and normal functions for Si-H and Si-H](image)

Figure 3.4. Comparison of the simplified angular function with the original function for Si.

The curves are indistinguishable for angles above 60°, with a maximum difference of 1.25% for very small angles. The alternate form of $g_{3\theta}(\theta)$ is therefore as valid as the original form, and makes the potential easier to evaluate. This especially important for force calculations, which are complicated by the inclusion of $H(N)$.

The new parameters for the potential were obtained by fitting to energies and bond lengths of various silicon hydride molecules and interstitial hydrogen sites in bulk silicon. The potential gives a reasonable description of gas phase species, except that the description of the Si-Si bond in disilene is poor due to an inadequate description of $\pi$ bonding. Hydrogen terminated surfaces are well
described. The predicted lengthening of the dimer bond to 2.43 Å on the one monolayer hydrogen \{100\}(2x1) surface is a similar to that reported in ab-initio calculations [128,129], and the H-Si-Si angle of 112.4° is in good agreement with reported values [130,131]. Repulsion between hydrogen atoms on the dihydride \{100\} surface results in symmetry breaking and a canted row structure is formed by all SiH₂ units rotating in the same direction. This is in qualitative agreement with ab-initio calculations [128], although the associated energy gain is somewhat underestimated. Hydrogen interstitials in silicon [132] are well described, and the description of bulk silicon and the reconstructed \{100\} silicon surface was shown to be good by Tersoff [97]. The potential is therefore suitable for simulations involving interaction with, and sputtering from, hydrogen terminated silicon surfaces. It may also be able to model some aspects of CVD growth of silicon. The new parameters for this potential were not systematically optimised, and no dynamic data was used in the fitting of the potential. The potential could therefore be improved by systematically refitting the parameters if enough reliable data were available. The description of small molecules, π bonding, and reconstructed surfaces could also be improved by the addition of correction terms such as those introduced by Brenner.

3.4.6 A New Empirical Potential for C-Si-H Systems

In order to extend simulations investigating the interaction of fullerenes with various crystal surfaces, it was proposed to examine the effects of hydrogen termination of silicon surfaces. Although no potential has been published for this three element system, all the elements necessary to produce such a potential are available. In particular, C/H interactions [65], C/Si interactions [102] and Si/H interactions [108] have been modelled using potentials based on Tersoff’s formalism by Brenner, Tersoff, and Murty and Atwater, respectively, as outlined in the precious sections. Here, the new C/Si/H potential and its complete parameter set are presented. The potential is constructed by a hybrid of the three potentials mentioned above, and to a large extent inherits their strengths and weaknesses. As the components of the potential have already been fit to available data and proven to be reliable a great deal of effort can be saved in the its production. Parameters for the potential are given in tables 3.1 to 3.8, unless otherwise indicated these values are taken from references [65,102,108].

Since this potential was produced, a similar C/Si/H potential has been developed by Dyson [133]. Dyson’s XB (eXtended Brenner) potential also uses the carbon and hydrogen parameters from Brenner’s C/H potential, with new parameters derived to model Si-Si, Si-C and Si-H interactions. Initial trials that we
conducted with Dyson's potential showed it to be seriously flawed. Dyson has since refitted the new parameters of the potential, but a complete testing still has to be conducted. The predictions of the 'hybrid' potential for $C_xSi_yH_z$ molecules (the only untested component of the potential) are presented at the end of the section. These are compared to predictions obtained using the latest parameterisation of Dyson's potential and to experimental results and ab-initio results.

The total potential energy is written as a sum over pairs

$$V = \sum_{i<j} \Phi_{ij}$$  \hspace{1cm} (3.4.35)

$$\Phi_{ij} = f_{ij}(r_{ij})[V_A(r_{ij}) - E_{ij}V_A(r_{ij})]$$  \hspace{1cm} (3.4.36)

The usual form of the cutoff function is used to restrict the potential to nearest neighbours for all interactions and is given by

$$f_{ij}(r_{ij}) = \begin{cases} 1, & r_{ij} \leq R_{ij}^{(1)} \\ 1 + \cos \left( \frac{\pi(r_{ij} - R_{ij}^{(1)})}{(R_{ij}^{(2)} - R_{ij}^{(1)})} \right) / 2, & R_{ij}^{(1)} < r_{ij} < R_{ij}^{(2)} \\ 0, & r_{ij} \geq R_{ij}^{(2)} \end{cases}$$  \hspace{1cm} (3.4.37)

The repulsive and attractive generalised Morse terms $V_R(r_{ij})$ and $V_A(r_{ij})$ are given by

$$V_R(r_{ij}) = A_{ij}F_1(N_{ij}^{(1)})\exp(-\lambda_{ij}r_{ij})$$  \hspace{1cm} (3.4.38)

$$V_A(r_{ij}) = B_{ij}F_2(N_{ij}^{(1)})\exp(-\mu_{ij}r_{ij})$$  \hspace{1cm} (3.4.39)

The functions $F_1$ and $F_2$ are those produced by Murty & Atwater for Si-H bonds and are functions of the coordination of the silicon atom. To obtain a continuous function for the coordination of the Si atom, it is written as

$$N_{ij}^{(1)} = \sum f_{ij}(r_{ij})$$  \hspace{1cm} (3.4.40)

The functions are given by cubic splines, fit to integer values of coordination from 1 through 4, with zero derivatives at the end points.

The bond order term is given by
where \( F_{cc} \) is Brenner's spline function that corrects for an overbinding of radicals and accounts for conjugation of \( C-C \) bonds in an approximate manner. The function is evaluated by tricubic interpolation between values at fit integer points.

The contribution from atom \( i \) to the bond order term is

\[
\bar{b}_y = \left[ b_y + b_{\mu} + F_{cc}(N_y^{(C)}, N_{ij}^{(C)}, N_{ij}^{(Si)}) \right]/2
\]

(3.4.41)

where \( H_y \) is obtained by bicubic interpolation between values fitted at integer points and is only used for \( C-C \) and \( C-H \) bonds. \( H_y \) is a correction produced by Brenner to account for the differing chemistry of \( C-C \) and \( C-H \) bonds. To extend the potential to the three element case, silicon must be accounted for in this function. The extension of this function to a tricubic spline of the form

\[
H_y' \left( N_y^{(H)}, N_y^{(C)}, N_y^{(Si)} \right)
\]

was considered, but there is insufficient data to fully parameterise this function. The original function has been retained, but silicon atoms are counted along with carbon atoms. As the chemistry of silicon and carbon is similar this is sufficient as a first approximation, but caution should be exercised where this may have a significant effect on calculations. The simulations conducted to date with the potential have only been concerned with low energy fullerene interactions with hydrogenated silicon surfaces, where this function has little effect.

The quantities \( N_i^{(C)} \), \( N_i^{(Si)} \), and \( N_i^{(H)} \) are the number of carbon, silicon and hydrogen atoms, respectively, that are bonded to atom \( i \), excluding atom \( j \).

\[
N_i^{(C)} = \sum_{k=\text{carbon}}^{k \neq j} f_{ik} (r_{ik}), \quad N_i^{(Si)} = \sum_{k=\text{silicon}}^{k \neq j} f_{ik} (r_{ik}), \quad N_i^{(H)} = \sum_{k=\text{hydrogen}}^{k \neq j} f_{ik} (r_{ik}) \quad (3.4.43)
\]

\( N_i^{(i)} \) is the total number of neighbours of atom \( i \), excluding atom \( j \).

\[
N_i^{(i)} = N_i^{(C)} + N_i^{(Si)} + N_i^{(H)} \quad (3.4.44)
\]

The effect of a carbon-carbon bond being part of a conjugated system is modelled by \( N_{ij}^{\text{conj}} \), where

\[
N_{ij}^{\text{conj}} = 1 + \sum_{\text{carbon} k \neq i} f_{ik} (r_{ik}) F(N_k^{(i)}) + \sum_{\text{carbon} k \neq j} f_{jk} (r_{jk}) F(N_j^{(j)}) \quad (3.4.45)
\]
and

\[ F(N_{ik}^{(i)}) = \begin{cases} 
1, & N_{ik}^{(i)} \leq 2 \\
\left(1 + \cos\left[\pi\left(N_{ik}^{(i)} - 2\right)\right]\right)/2, & 2 < N_{ik}^{(i)} < 3 \\
0, & N_{ik}^{(i)} \geq 3 
\end{cases} \]  (3.4.46)

For simplicity, silicon neighbours are assumed to have no effect on the conjugation of C-C bonds.

Competition between bonds is described by

\[ \zeta_{ij} = \sum_{k \neq i,j} f_{ij}(r_{ik}) g_{ij}(\theta_{jk}) \exp\left[\alpha\left\{\left(r_{ij} - R_{ij}^{(e)}\right) - \left(r_{ik} - R_{ik}^{(e)}\right)\right\}\right] \]  (3.4.47)

Depending upon the type of atoms \(i, j\) and \(k\), several parameterisations are used for the exponential term and different functional forms are used for the angle dependent term. These are given in tables 3.2 to 3.5. For \(i=carbon\), two parameterisations of the function

\[ g_{c}(\theta) = a\left[1 + c\sqrt{d^2 - c^2}(d^2 + (h - \cos\theta)^2)\right] \]  (3.4.48)

are used. If \(j\) is silicon, the parameters produced by Tersoff are used, otherwise those from the first parameterisation of Brenner’s potential are applied. For \(i=silicon\), two parameterisations of the function

\[ g_{si}(\theta) = c + d\left[H\left(N_{si}^{(i)}\right) - \cos\theta\right]^2 \]  (3.4.49)

are used. If \(j\) and \(k\) are carbon or silicon, a parameterisation equivalent to Tersoff’s term for silicon is used, with the function \(H(N)\) replaced by a constant. If either \(j\) or \(k\) is hydrogen, the parameters given by Murty & Atwater are used and \(H(N)\) is given by a cubic spline. For \(i=hydrogen\), two parameterisations of the function

\[ g_{h}(\theta) = c + d\left(h - \cos\theta\right)^2 \]  (3.4.50)

are used. One corresponds to the usual case of monovalent hydrogen and is given in the first parameterisation of Brenner’s potential, the other was produced by Murty & Atwater to allow for bond-centred hydrogen.
In its present form, the potential is designed to reduce to Brenner's hydrocarbon potential in the absence of silicon, and to reduce to Murty and Atwater's potential if there is no carbon present. The $Si/H$ potential allows the presence of bond-centred hydrogen interstitials in silicon, whereas Brenner's potential does not account for such interstitials in diamond although they are known to occur [134]. The inclusion of a term to model bond-centred hydrogen interstitials in $Si$ also allows bond-centred hydrogen to occur on the silicon surface, but there is less experimental evidence to support this. The hybrid potential was kept in the present form to conduct simulations of $C_60$ interacting with hydrogenated silicon surfaces. If bond-centred hydrogen were allowed to occur in carbon and silicon carbide, then there is the possibility of a fullerene becoming bound to the silicon surface via one or more hydrogen centred bonds. To preclude such unlikely events from occurring the potential is chosen to prevent $C-H-C$ and $C-H-Si$ bonds from forming by using Brenner's expression for $g_{ij}(\theta)$ in these cases. Murty and Atwater's alternative expression is used to allow displaced hydrogen atoms to become interstitials within the silicon substrate by the formation of $Si-H-Si$ bonds. For more general applications the same parameters should be used for the angular term in $C-H-C$, $C-H-Si$ and $Si-H-Si$ environments, although the choice between allowing bond-centred hydrogen or not will depend upon the type of simulation being conducted.

Tables 3.1 to 3.8 give the values of all parameters used in the potential and references to their original publication. Some parameters are derived from earlier potentials, but rewritten to fit the notation used above to describe this potential. Any parameters not obtained from other potentials are indicated.

<table>
<thead>
<tr>
<th></th>
<th>$C-C$ [65]</th>
<th>$C-Si$ [102]</th>
<th>$C-H$ [65]</th>
<th>$Si-Si$ [102]</th>
<th>$Si-H$ [108]</th>
<th>$H-H$ [65]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ (eV)</td>
<td>518.3696</td>
<td>1597.311</td>
<td>294.4519</td>
<td>1830.800</td>
<td>323.5400</td>
<td>80.07035</td>
</tr>
<tr>
<td>$B$ (eV)</td>
<td>328.0206</td>
<td>395.1451</td>
<td>90.09490</td>
<td>471.1800</td>
<td>84.18000</td>
<td>31.37934</td>
</tr>
<tr>
<td>$\lambda$ (Å⁻¹)</td>
<td>2.409357</td>
<td>2.983900</td>
<td>3.651691</td>
<td>2.479900</td>
<td>2.959500</td>
<td>4.207524</td>
</tr>
<tr>
<td>$\mu$ (Å⁻¹)</td>
<td>1.867718</td>
<td>1.972050</td>
<td>2.100363</td>
<td>1.732200</td>
<td>1.615800</td>
<td>1.795632</td>
</tr>
<tr>
<td>$R^{(e)}$ (Å)</td>
<td>1.315</td>
<td>1.85⁹</td>
<td>1.1199</td>
<td>2.35</td>
<td>1.475</td>
<td>0.74</td>
</tr>
<tr>
<td>$R^{(n)}$ (Å)</td>
<td>1.7</td>
<td>2.204541</td>
<td>1.3</td>
<td>2.7</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>$R^{(s)}$ (Å)</td>
<td>2.0</td>
<td>2.509980</td>
<td>1.8</td>
<td>3.0</td>
<td>2.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 3.1. Parameters for the pairwise components of the potential.

*For $Si-C$, $R^{(e)}$ was chosen as the mean of the dimer bond length [135] and the bond length in the zinc blende structure[102].
Figure 3.5. Definition of atoms $i$, $j$ and $k$ as used in Table 3.2.

<table>
<thead>
<tr>
<th>$j$</th>
<th>$i$</th>
<th>$k$</th>
<th>$\eta, \delta$</th>
<th>$g(\theta)$</th>
<th>$\exp(r_{ij} - r_{ik})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$</td>
<td>$C$</td>
<td>C, Si or H</td>
<td>$C_{\text{Brenner}}$</td>
<td>$C_{\text{Brenner}}$</td>
<td>none</td>
</tr>
<tr>
<td>$Si$</td>
<td>$C$</td>
<td>C, Si or H</td>
<td>$C_{\text{Tersoff}}$</td>
<td>$C_{\text{Tersoff}}$</td>
<td>none</td>
</tr>
<tr>
<td>$H$</td>
<td>$C$</td>
<td>C or Si</td>
<td>$C_{\text{Brenner}}$</td>
<td>$C_{\text{Brenner}}$</td>
<td>none</td>
</tr>
<tr>
<td>$H$</td>
<td>$C$</td>
<td>$H$</td>
<td>$C_{\text{Brenner}}$</td>
<td>$C_{\text{Brenner}}$</td>
<td>$C_{\text{Brenner}}$</td>
</tr>
<tr>
<td>$C$</td>
<td>$Si$</td>
<td>C or Si</td>
<td>$Si_{\text{Tersoff}}$</td>
<td>$Si_{\text{Tersoff}}$</td>
<td>none</td>
</tr>
<tr>
<td>$C$</td>
<td>$Si$</td>
<td>$H$</td>
<td>$Si_{\text{Tersoff}}$</td>
<td>$Si_{\text{Murty}}$</td>
<td>$Si_{\text{Murty}}$</td>
</tr>
<tr>
<td>$Si$</td>
<td>$Si$</td>
<td>C</td>
<td>$Si_{\text{Tersoff}}$</td>
<td>$Si_{\text{Tersoff}}$</td>
<td>none</td>
</tr>
<tr>
<td>$Si$</td>
<td>$Si$</td>
<td>Si</td>
<td>$Si_{\text{Tersoff}}$</td>
<td>$Si_{\text{Tersoff}}$</td>
<td>$Si_{\text{Tersoff}}$</td>
</tr>
<tr>
<td>$Si$</td>
<td>$Si$</td>
<td>$H$</td>
<td>$Si_{\text{Tersoff}}$</td>
<td>$Si_{\text{Murty}}$</td>
<td>$Si_{\text{Murty}}$</td>
</tr>
<tr>
<td>$H$</td>
<td>$Si$</td>
<td>C, Si or H</td>
<td>$Si_{\text{Murty}}$</td>
<td>$Si_{\text{Murty}}$</td>
<td>$Si_{\text{Murty}}$</td>
</tr>
<tr>
<td>$C$</td>
<td>$H$</td>
<td>C or Si</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
</tr>
<tr>
<td>$C$</td>
<td>$H$</td>
<td>$H$</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
</tr>
<tr>
<td>$Si$</td>
<td>$H$</td>
<td>$C$</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
</tr>
<tr>
<td>$Si$</td>
<td>$H$</td>
<td>Si</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Murty}}$</td>
<td>none</td>
</tr>
<tr>
<td>$Si$</td>
<td>$H$</td>
<td>$H$</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
</tr>
<tr>
<td>$H$</td>
<td>$H$</td>
<td>C, Si or H</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
<td>$H_{\text{Brenner}}$</td>
</tr>
</tbody>
</table>

Table 3.2. Scheme for selection of the many-body parameters given in tables 3.3 to 3.5.

The choice of parameters for these expression specifies whether or not bond-centred hydrogen is allowed. The current parameterisation only allows bond-centred hydrogen between two silicon atoms. Using Murty and Atwater's alternative parameterisation for the bond angle term and no length term in all three cases will also allow bond-centred hydrogen in carbon and mixed environments. Alternatively, to prevent hydrogen-centred bonds, Brenner's parameterisation can be used for all cases.
<table>
<thead>
<tr>
<th></th>
<th>$C_{\text{Brenner}}$ [65]</th>
<th>$C_{\text{Tersoff}}$ [102]</th>
<th>$S_{\text{Tersoff}}$ [102]</th>
<th>$S_{\text{Murty}}$ [108]</th>
<th>$H_{\text{Brenner}}$ [65]</th>
<th>$H_{\text{Murty}}$ [108]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>1.0</td>
<td>0.72752</td>
<td>0.78734</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.80469</td>
<td>0.687276</td>
<td>0.635050</td>
<td>0.80469</td>
<td>0.80469</td>
<td>0.80469</td>
</tr>
</tbody>
</table>

Table 3.3. Values for $\eta$ and $\delta$.

<table>
<thead>
<tr>
<th></th>
<th>$C_{\text{Brenner}}$ [65]</th>
<th>$C_{\text{Tersoff}}$ [102]</th>
<th>$S_{\text{Tersoff}}$ [102]</th>
<th>$S_{\text{Murty}}$ [108]</th>
<th>$H_{\text{Brenner}}$ [65]</th>
<th>$H_{\text{Murty}}$ [108]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>0.011304</td>
<td>1.5724x10^{-7}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$c$</td>
<td>19.0</td>
<td>3.8049x10^{-4}</td>
<td>0.0</td>
<td>0.0216</td>
<td>4.0</td>
<td>0.700</td>
</tr>
<tr>
<td>$d$</td>
<td>2.5</td>
<td>4.384</td>
<td>0.16</td>
<td>0.27</td>
<td>0.0</td>
<td>1.00</td>
</tr>
<tr>
<td>$h$</td>
<td>-1.0</td>
<td>-0.57058</td>
<td>-0.59826</td>
<td>$H(N)$</td>
<td>-</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

Table 3.4. Parameters for the bond angle functions.

<table>
<thead>
<tr>
<th></th>
<th>$C_{\text{Brenner}}$ [65]</th>
<th>$S_{\text{Tersoff}}$ [102]</th>
<th>$S_{\text{Murty}}$ [108]</th>
<th>$H_{\text{Brenner}}$ [65]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ (Å$^{-1}$ or Å$^{-3}$)</td>
<td>3.0</td>
<td>5.197495</td>
<td>4.0</td>
<td>3.0</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.5. Parameters for bond length terms.

Tables 3.6 to 3.8 give the values used at integer points to produce the spline functions used in the potential. The data in table 3.6 is taken from reference [108] and is used to create cubic splines with zero first derivative at $N=1$ and $N=4$. Tables 3.7 and 3.8 give data from reference [65]. A continuous function is obtained by tricubic and bicubic interpolation using the function values and derivatives.

<table>
<thead>
<tr>
<th></th>
<th>$F_1(N)$</th>
<th>$F_2(N)$</th>
<th>$H(N)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.005</td>
<td>0.930</td>
<td>-0.040</td>
</tr>
<tr>
<td>2</td>
<td>1.109</td>
<td>1.035</td>
<td>-0.040</td>
</tr>
<tr>
<td>3</td>
<td>0.953</td>
<td>0.934</td>
<td>-0.276</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
<td>1.000</td>
<td>-0.470</td>
</tr>
</tbody>
</table>

Table 3.6. The cubic spline functions for the Si-H potential.
Table 3.7. Values for \( F_{cc} \) and derivatives at integer points.

\( F_{cc}(y,x,z) = F_{cc}(x,y,z) \) and \( \partial F_{cc}(y,x,z)/\partial x = \partial F_{cc}(x,y,z)/\partial x \), all other values are zero. \( F_{cc}(x,y,z > 2) = F_{cc}(x,y,2) \).

*Note that \( F_{cc}(2,3,2) \) and \( \partial F_{cc}(1,3,2)/\partial N^{(t)}_q \) are assigned different values to those given by Brenner, to improve the description atom fullerene interactions. This is described in more detail in section 3.8.4. The original values are -0.0465 and 0.03755 respectively.
Table 3.8. Values for $H_{cc}$, $H_{cu}$ and derivatives at integer points. All values not given are equal to zero.

<table>
<thead>
<tr>
<th>$H_{cc}(x,y)$</th>
<th>$H_{cu}(x,y)$</th>
<th>$\partial H_{cu}/\partial x$</th>
<th>$\partial H_{cu}/\partial y$</th>
<th>$x$</th>
<th>$y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-0.1792</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>-</td>
<td>-0.2407</td>
<td>-</td>
<td>-0.07655</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>-</td>
<td>-0.3323</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>-</td>
<td>-0.0760</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>-0.0175</td>
<td>-0.2477</td>
<td>-0.07640</td>
<td>-0.12805</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0.0115</td>
<td>-0.3321</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>-0.0070</td>
<td>-0.2163</td>
<td>-0.13075</td>
<td>-</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>0.0118</td>
<td>-0.3320</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>0.0119</td>
<td>-0.3375</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

The individual components of the potential have already been examined by their respective developers. The description of bulk silicon and silicon carbide was validated by Tersoff [97,102]. Similarly, Brenner [65] has given results for the description of bulk allotropes of carbon. The properties of gas phase hydrocarbon and hydrosilicon molecules and hydrogen terminated surfaces have been tested by Brenner [65] and Murty & Atwater [108]. Hence, the only component of the potential that is untested is the description of mixed hydride molecules. Unfortunately there is little experimental data on the structures and more importantly the heats of formation of these molecules, so results of ab-initio calculations are also used for the testing. The following tables give the predicted properties of some molecules whose energy and structure has been determined. The data for each molecule was obtained by a steepest descent optimisation, starting from an approximate structure. The results from Dyson’s XB potential are also shown for comparison. Atomisation energies were determined from Heats of formation using cohesive energies for carbon, silicon and hydrogen of 7.3768 eV, 4.63 eV and 2.375 eV, respectively. In table 3.9 the descriptions of various organosilanes, where carbon atom of the $Si-C$ bond is either $sp^3$, $sp^2$, or $sp$ hybridised are examined. Table 3.10 examines the predictions for the structures and energies of the isomers of $SiCH_4$. 

83
<table>
<thead>
<tr>
<th></th>
<th>'Hybrid' potential</th>
<th>XB potential</th>
<th>Expt. / Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{SiH}_3 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_{C-H} )</td>
<td>1.073 Å</td>
<td>1.069 Å</td>
<td>1.093 Å</td>
</tr>
<tr>
<td>( \theta_{H-C-H} )</td>
<td>105.9°</td>
<td>111.7°</td>
<td>107.7°</td>
</tr>
<tr>
<td>( R_{C-Si} )</td>
<td>1.872 Å</td>
<td>1.879 Å</td>
<td>1.867 Å</td>
</tr>
<tr>
<td>( R_{Si-H} )</td>
<td>1.475 Å</td>
<td>1.480 Å</td>
<td>1.485 Å</td>
</tr>
<tr>
<td>( \theta_{H-Si-H} )</td>
<td>109.0°</td>
<td>105.3°</td>
<td>108.3°</td>
</tr>
<tr>
<td>( E_{\text{Atomisation}} )</td>
<td>26.3 eV</td>
<td>25.3 eV</td>
<td>26.4 eV</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{SiH}_3 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{\text{Atomisation}} )</td>
<td>38.6 eV</td>
<td>37.6 eV</td>
<td>39.6 eV</td>
</tr>
<tr>
<td>( \text{CH}_2\text{CHSiH}_3 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_{C-H} )</td>
<td>1.071 Å</td>
<td>1.070 Å</td>
<td>1.097 Å</td>
</tr>
<tr>
<td>( \theta_{H-C-C} )</td>
<td>123.7°</td>
<td>123.8°</td>
<td>120.5°†</td>
</tr>
<tr>
<td>( R_{C-C} )</td>
<td>1.324 Å</td>
<td>1.316 Å</td>
<td>1.347 Å</td>
</tr>
<tr>
<td>( \theta_{C-C-H} )</td>
<td>118.7°</td>
<td>125.5°</td>
<td>118.0°</td>
</tr>
<tr>
<td>( \theta_{C-Si-C} )</td>
<td>121.6°</td>
<td>124.0°</td>
<td>122.8°</td>
</tr>
<tr>
<td>( R_{C-H} )</td>
<td>1.071 Å</td>
<td>1.073 Å</td>
<td>1.094 Å</td>
</tr>
<tr>
<td>( R_{C-Si} )</td>
<td>1.836 Å</td>
<td>1.838 Å</td>
<td>1.853 Å</td>
</tr>
<tr>
<td>( R_{Si-H} )</td>
<td>1.475 Å</td>
<td>1.482 Å</td>
<td>1.475 Å</td>
</tr>
<tr>
<td>( \theta_{H-Si-H} )</td>
<td>108.9°</td>
<td>104.4°</td>
<td>108.7°</td>
</tr>
<tr>
<td>( E_{\text{Atomisation}} )</td>
<td>32.9 eV</td>
<td>31.8 eV</td>
<td>33.5 eV</td>
</tr>
<tr>
<td>( \text{CHCSiH}_3 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_{C-H} )</td>
<td>1.070 Å</td>
<td>1.070 Å</td>
<td>1.056 Å</td>
</tr>
<tr>
<td>( R_{C-C} )</td>
<td>1.207 Å</td>
<td>1.196 Å</td>
<td>1.208 Å</td>
</tr>
<tr>
<td>( R_{C-Si} )</td>
<td>1.832 Å</td>
<td>1.805 Å</td>
<td>1.826 Å</td>
</tr>
<tr>
<td>( R_{Si-H} )</td>
<td>1.475 Å</td>
<td>1.482 Å</td>
<td>1.455 Å</td>
</tr>
<tr>
<td>( \theta_{H-Si-H} )</td>
<td>108.9°</td>
<td>103.5°</td>
<td>110.3°</td>
</tr>
<tr>
<td>( E_{\text{Atomisation}} )</td>
<td>26.3 eV</td>
<td>25.6 eV</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.9. Properties of some \( X-\text{SiH}_3 \) molecules.

a Structural information obtained by experiment; taken from [136].
b Structural information obtained by experiment; taken from [137].
c Structural information obtained by experiment; taken from [138].
α Heat of formation obtained by experiment; taken from [139].
β Heat of formation obtained by experiment; taken from [140].
† Average of two slightly different values.
Table 3.10. Properties of some isomers of CSiH₄.

<table>
<thead>
<tr>
<th></th>
<th>‘Hybrid’ potential</th>
<th>XB potential</th>
<th>Expt. / Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂SiH₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rₐ-H</td>
<td>1.069 Å</td>
<td>1.068 Å</td>
<td>1.075 Å</td>
</tr>
<tr>
<td>θₐ-H-C-H</td>
<td>115.8°</td>
<td>121.6°</td>
<td>115.0°</td>
</tr>
<tr>
<td>Rₛ-Si</td>
<td>1.818 Å</td>
<td>1.809 Å</td>
<td>1.715 Å</td>
</tr>
<tr>
<td>Rₛ-H</td>
<td>1.480 Å</td>
<td>1.461 Å</td>
<td>1.474 Å</td>
</tr>
<tr>
<td>θₛ-Si-H</td>
<td>106.0°</td>
<td>112.5°</td>
<td>115.1°</td>
</tr>
<tr>
<td>EₐAtomisation</td>
<td>18.8 eV</td>
<td>19.1 eV</td>
<td>19.7 eV</td>
</tr>
<tr>
<td>CH₃SiH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rₐ-H</td>
<td>1.074 Å</td>
<td>1.069 Å</td>
<td>1.087 Å</td>
</tr>
<tr>
<td>θₐ-H-Si</td>
<td>113.4°</td>
<td>107.6°</td>
<td>111.2°</td>
</tr>
<tr>
<td>Rₛ-Si</td>
<td>1.844 Å</td>
<td>1.826 Å</td>
<td>1.934 Å</td>
</tr>
<tr>
<td>θₛ-Si-H</td>
<td>92.3°</td>
<td>179.7°</td>
<td>95.9°</td>
</tr>
<tr>
<td>Rₛ-H</td>
<td>1.510 Å</td>
<td>1.443 Å</td>
<td>1.534 Å</td>
</tr>
<tr>
<td>EₐAtomisation</td>
<td>19.7 eV</td>
<td>20.2 eV</td>
<td>19.4 eV</td>
</tr>
<tr>
<td>CHSiH₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rₐ-H</td>
<td>1.076 Å</td>
<td>1.070 Å</td>
<td>1.076 Å</td>
</tr>
<tr>
<td>θₐ-H-Si</td>
<td>125.3°</td>
<td>179.6°</td>
<td>139.5°</td>
</tr>
<tr>
<td>Rₛ-Si</td>
<td>1.829 Å</td>
<td>1.806 Å</td>
<td>1.871 Å</td>
</tr>
<tr>
<td>θₛ-Si-H</td>
<td>110.1°</td>
<td>114.9°</td>
<td>110.1°</td>
</tr>
<tr>
<td>Rₛ-H</td>
<td>1.475 Å</td>
<td>1.482 Å</td>
<td>1.484 Å</td>
</tr>
<tr>
<td>EₐAtomisation</td>
<td>18.0 eV</td>
<td>17.2 eV</td>
<td>17.5 eV</td>
</tr>
</tbody>
</table>

Table 3.10. Properties of some isomers of CSiH₄.

<table>
<thead>
<tr>
<th></th>
<th>‘Hybrid’ potential</th>
<th>XB potential</th>
<th>Expt. / Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂SiH₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rₐ-H</td>
<td>1.069 Å</td>
<td>1.068 Å</td>
<td>1.075 Å</td>
</tr>
<tr>
<td>θₐ-H-C-H</td>
<td>115.8°</td>
<td>121.6°</td>
<td>115.0°</td>
</tr>
<tr>
<td>Rₛ-Si</td>
<td>1.818 Å</td>
<td>1.809 Å</td>
<td>1.715 Å</td>
</tr>
<tr>
<td>Rₛ-H</td>
<td>1.480 Å</td>
<td>1.461 Å</td>
<td>1.474 Å</td>
</tr>
<tr>
<td>θₛ-Si-H</td>
<td>106.0°</td>
<td>112.5°</td>
<td>115.1°</td>
</tr>
<tr>
<td>EₐAtomisation</td>
<td>18.8 eV</td>
<td>19.1 eV</td>
<td>19.7 eV</td>
</tr>
<tr>
<td>CH₃SiH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rₐ-H</td>
<td>1.074 Å</td>
<td>1.069 Å</td>
<td>1.087 Å</td>
</tr>
<tr>
<td>θₐ-H-Si</td>
<td>113.4°</td>
<td>107.6°</td>
<td>111.2°</td>
</tr>
<tr>
<td>Rₛ-Si</td>
<td>1.844 Å</td>
<td>1.826 Å</td>
<td>1.934 Å</td>
</tr>
<tr>
<td>θₛ-Si-H</td>
<td>92.3°</td>
<td>179.7°</td>
<td>95.9°</td>
</tr>
<tr>
<td>Rₛ-H</td>
<td>1.510 Å</td>
<td>1.443 Å</td>
<td>1.534 Å</td>
</tr>
<tr>
<td>EₐAtomisation</td>
<td>19.7 eV</td>
<td>20.2 eV</td>
<td>19.4 eV</td>
</tr>
<tr>
<td>CHSiH₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rₐ-H</td>
<td>1.076 Å</td>
<td>1.070 Å</td>
<td>1.076 Å</td>
</tr>
<tr>
<td>θₐ-H-Si</td>
<td>125.3°</td>
<td>179.6°</td>
<td>139.5°</td>
</tr>
<tr>
<td>Rₛ-Si</td>
<td>1.829 Å</td>
<td>1.806 Å</td>
<td>1.871 Å</td>
</tr>
<tr>
<td>θₛ-Si-H</td>
<td>110.1°</td>
<td>114.9°</td>
<td>110.1°</td>
</tr>
<tr>
<td>Rₛ-H</td>
<td>1.475 Å</td>
<td>1.482 Å</td>
<td>1.484 Å</td>
</tr>
<tr>
<td>EₐAtomisation</td>
<td>18.0 eV</td>
<td>17.2 eV</td>
<td>17.5 eV</td>
</tr>
</tbody>
</table>

The results from table 3.9 show that the new potential function provides a good description of both the structure and energy of organosilane molecules. In all four cases considered, the predicted structure and energy of the molecule is better than given by the XB potential. The worst case is ethylsilane, where the atomisation energy is underestimated by 1.0 eV (0.09 eV/atom). The molecules examined in table 3.10 should offer a tougher test of the potential as large changes occur in the coordination of the C and Si atoms. Ab-initio calculations [141] give the energies relative to silaethylene as -0.017 eV and +1.93 eV for methylsilylene and silylmethylene, respectively, while experiment [139] gives a value of +0.3 eV for methylsilylene relative to silaethylene. As no experimental value was available.
for the atomisation energy of silylmethylene, it was estimated using the calculated energy difference between methylsilylene and silylmethylene, together with the experimental value for methylsilylene. The hybrid potential gives a good prediction of the structures, but gives an atomisation energy that is 0.9 eV too low for silaethylene. This error is probably due to a poor description of the carbon-silicon double bond. The other energies are given to a reasonable accuracy, and the difference between methylsilylene and silylmethylene values (1.7 eV) is much closer to the \textit{ab-initio} value (1.9 eV) than the XB value (3.0 eV).

Considering that the parameters describing the C-Si bond were only fit to the cohesive energy of silicon carbide, the agreement with experimental values is very good, illustrating the transferability of Tersoff-type potentials. The fact that the 'hybrid' potential consistently performs better than the XB potential is a little surprising, as the latter potential was specifically formulated to model the interaction of hydrocarbon molecules with silicon surfaces. The inclusion of correction terms for silicon-hydrogen bonds in the Murty & Atwater potential must be partly responsible for the greater accuracy in the hybrid potential. The potential could still be improved by the addition of correction terms, similar to those used in the Brenner potential, for C-Si and Si-Si bonds, although it is unclear if sufficient reliable data exists to achieve this.
3.5 Heggie’s Proximity Cell Potential for Carbon

3.5.1 The Basis of the Potential

An alternative to the Tersoff-type empirical potentials for carbon has been produced by Heggie [58]. Although Heggie’s potential has only been applied in a small proportion of the work presented in this thesis, a detailed description is included here, because several errors were discovered in reference [58] during implementation of the potential. The parameter set is not presented here, as it is given correctly in reference [58]. The potential differs from the majority of empirical potentials, as the potential energy of an atom is written explicitly as a function of the local environment, rather than a functional of pair and bond-angle terms. The arbitrary cutoff distance that is necessary to restrict interactions to nearest neighbours in Tersoff-type potentials is not required. It is replaced by a more general cutoff based on both the bond length and the amount of ‘space’ available for the bond. Hence, the potential can describe the interaction between differing layers in the graphite structure, which is ignored by Tersoff-type potentials. The potential is based on the Wigner-Seitz cell (also known as the proximity cell or Voronoi polyhedron) of each atom. The proximity cell of an atom encloses the region of space closer to that atom than any other.

There are some situations where the potential cannot be expected to give reliable results. It was only designed to model sp$^2$ and sp$^3$ hybridised atoms, and so does not give a good description of low coordinated carbon atoms. The major motivation in the design of the potential was the study of defects and interstitials in graphite and diamond, so it was not necessary for the potential to model surfaces or large interlayer separation in graphite. Hence the applicability of the potential is limited in some situations. There is a second problem with the description of interlayer forces in graphite. The stacking potential was fit to give the correct cohesive energy and elastic constants for the perfect graphite structure. This was achieved, but the minimum energy structure predicted by the potential is not the perfect graphite structure, instead the potential gives a slightly buckled graphite plane.

A major drawback of basing the potential on proximity cells of atoms is that it cannot be differentiated analytically. The complicated form of the potential and the necessity of creating the Voronoi polyhedron for each atom, coupled with the far greater number of evaluations required due to the long-ranged nature of the potential and the need to use numerical differentiation, make the potential at least an order of magnitude slower than Tersoff-type potentials.
3.5.2 The Potential

The local environment of each atom is 'measured' via the construction of the proximity cell for that atom. Each face of the proximity cell corresponds to a possible bond on the atom. The strength of each bond is determined by the bond length and geometric parameters calculated for the face of the cell associated with that bond. A screening function is used to cut interactions off smoothly; this is a generalisation of the cosine cutoff function used in Tersoff type potentials that allows the endpoints to vary. The parameters $a_i$ and $a_u$ determine the position and steepness of the cutoff.

$$f(a,a_i,a_u) = \begin{cases} 
0, & a \leq a_i \\
1 + \cos \left( \frac{\pi(a-a_i)}{(a_u-a_i)} \right) & 2a_i < a < a_u \\
1, & a \geq a_u 
\end{cases} \quad (3.5.1)$$

The potential involves three internal degrees of freedom for each atom, represented as a vector $\mathbf{p}_i$, defining the magnitude and direction of the unhybridised $p$ orbital of each atom. For sp$^3$ hybridised atoms, $|\mathbf{p}_i|$ is zero and for sp$^2$ hybridised atoms it has a maximum value of one. The potential does not account for atoms that may be in other hybridisation states. The $p$ vector of an atom is used to calculate atom centred parameters reflecting the hybridisation state of the atom. The strength of each bond is also affected by a bond centred parameter that is dependent upon the hybridisation of the atoms involved and the local environment.

For each bond between atoms $i$ and $j$, two further vectors are defined by

$$\mathbf{p}_i' = \mathbf{p}_i - (\mathbf{p}_i \cdot \hat{r}_{ij})\hat{r}_{ij} \quad (3.5.2)$$

$$\mathbf{p}_j'' = (\mathbf{p}_j \cdot \hat{p}_i'')\hat{p}_i''$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ is the internuclear vector between atoms $i$ and $j$. Thus $\mathbf{p}_i'$ is the projection of $\mathbf{p}_i$ onto the face of the cell that represents the bond between $i$ and $j$, whilst $\mathbf{p}_j''$ is the projection of $\mathbf{p}_j$ onto $\mathbf{p}_i'$. These two vectors are used to determine whether a bond has $\pi$ or $\sigma$ character.

Two $\phi$ parameters, one atom centred and one bond centred, are used in interpolation functions. The atom centred parameter for atom $i$ is given by
\[ \phi_i = f\left(\|p_i\|, 0.1\right) \]  
(3.5.3)

and defines the hybridisation state of the atom. For each bond between atoms \( i \) and \( j \), the bond centred parameter \( \phi_{ij} \) is given by

\[ \phi_{ij} = \left( \frac{1}{4} r^{-4} + \frac{1}{4} |p_{ij}|^{-4} + \frac{1}{2} |p_{ij}'|^{-4} \right)^{\frac{1}{4}} \]  
(3.5.4)

where

\[ r = f(\Delta_{ij}, \Delta_i, \Delta_j) \left[ p_i \cdot p_j \|p_{ij}'\| (2 - |p_{ij}|)(2 - |p_{ij}'|) \right]^4 \]  
(3.5.5)

and

\[ \Delta_{ij} = r_{\sigma_0} + \sqrt{2 \delta_{ij}^2 2 \delta_{ij}' / (\delta_{ij}^2 + \delta_{ij}'^2)} \quad \text{where} \quad \delta_{ij} = \Delta_{ij} - r_{\sigma_0} \]
\[ \delta_{ij}' = \Delta_{ij}' - r_{\sigma_0} \]  
(3.5.6)

The value of \( \phi_{ij} \) lies between zero and one and is small unless both atoms \( i \) and \( j \) are sp\(^2\) hybridised and in a geometry that allows \( \pi \) bonding. The quantities \( \Delta_{ij}, \Delta_{ij}' \) and \( r_{\sigma_0} \) are the three geometric parameters for the face. The ‘area’ of the face is represented by \( r_{\sigma_0} \); this is used to determine if the bond is screened due to intervening atoms. The elongation of the face in the direction of any unhybridised \( p \) orbital on the atom is measured by \( \Delta_{ij} \) and \( \Delta_{ij}' \). Note that equation (3.5.5) is a correction to reference [58].

To enable the potential to accurately describe diamond and graphite, parameters were first fit to data from each structure. In the potential, these parameters are represented by functions of the form

\[ h(\phi) = (1 - \phi)h(0) + \phi h(1) \]  
(3.5.7)

that linearly interpolate between the diamond (\( \phi = 0 \)) and graphite (\( \phi = 1 \)) values.

The total potential energy of a system is written as a sum over atoms

\[ V = \sum_i V_i \]  
(3.5.8)

\[ V_i = -V_e + \sum_{\text{all faces}} \left( (V_r)_{ij} + (V_r')_{ij} \right) + V_K - V_e + V'_e \]  
(3.5.9)
The reference energy is given by $V_0$, $V_r$, and $V_a$ are the repulsive and attractive parts of a Morse-like potential, $V_k$ is a Keating-like bond-bending potential. The repulsive and attractive parts of an interlayer potential for graphite are represented by $V_r^*$ and $V_a^*$. The repulsive terms are summed over all faces of the proximity cell, while the Keating term and the attractive Morse term are only summed for those terms deemed to be covalent bonds, i.e. the four best faces for bonding. The attractive part of the interlayer term acts between $\pi$ systems in different layers and so is summed only for the three best covalent bonds. Note that equation (3.5.9) is a correction to reference [58].

The Morse-like repulsive term for each face is

$$
(V_r)_{ij} = \frac{1}{2} a_i \big( \phi_{ij} \big) \left[ 1 - f \left( r_{ij}, r_i, r_j \right) \right] f \left( 2 r_i / r_{ij}, \phi_i \left( \phi_{ij} \right), \phi_j \left( \phi_{ij} \right) \right) \exp \left[ -\alpha_i \left( \phi_{ij} \right) r_{ij} \right] \quad (3.5.10)
$$

This is basically an exponential function, but the interaction cuts off as the bond-length becomes too great or the area of the face becomes too small. Also, the parameters $a, \alpha_i, \theta_i, \theta_a$ for the exponential and cutoff functions are dependent upon the bond-centred parameter $\phi_{ij}$.

Similarly, the Morse-like attractive term for a face is

$$
d_{ij} = \frac{1}{2} b_i \left( \phi_{ij}^* \right) f \left( 2 r_i / r_{ij}, \phi_i \left( \phi_{ij} \right), \phi_j \left( \phi_{ij} \right) \right) \exp \left[ -\alpha_i \left( \phi_{ij} \right) r_{ij} \right] \quad (3.5.11)
$$

with coupling between the interlayer distance and in-plane bonding achieved by a modification of $\phi_{ij}$ for the first term in the expression. This modification is given as

$$
\phi_{ij}^* = \phi_{ij} \left( 1 - \left[ \Delta_{ij} + \Delta_{ij} - c/2 \right] s_1 - \left[ \Delta_{ij} - c/4 \right] s_2 - \left[ \Delta_{ij} - c/4 \right] s_2 \right) \quad (3.5.12)
$$

where $c/2$ is the graphite interlayer separation of 3.35 Å. The modification of $\phi_{ij}$ for the first term in equation (3.5.11) was not made apparent in reference [58]. As carbon can form a maximum of four covalent bonds under $sp^3$ hybridisation and a maximum of three bonds under $sp^2$ hybridisation, only the four faces with maximum $d_{ij}$ are considered. If the atom is not completely $sp^3$ hybridised, these bond energies are modified to give three basically $sp^2$ bonds of strength $d_{ij}'$ and one weak bond of strength $d_{ij}''$ using the unhybridised p orbital, where

$$
d_{ij}' = d_{ij} \left( 1 - \phi_{ij}^* \right) \quad d_{ij}'' = d_{ij} \left[ 1 - \phi_{ij} \left( 1 - \phi_{ij}^* \right) \right] \quad (3.5.13)
$$
and

$$t'_j = f\left(\mathbf{p}_i \cdot \mathbf{r}_j, 0.05, 0.95\right)$$  \hspace{1cm} (3.5.14)$$

Equation (3.5.14) is a correction to reference [58]. Three bonds of strength $d'_{ij}$ and one bond of strength $d''_{ij}$ are chosen so that the covalent bonding energy is maximised, giving

$$V_a = d'_{ia} + d'_{ib} + d'_{ic} + d''_{id}$$  \hspace{1cm} (3.5.15)$$

The Keating-like term is given by

$$V_K = s^K(\phi) \left( \sum_{j,a} d^K_{ja} \left( r_{ja} \cdot r_a - r_a(\phi)^2 c^K(\phi) \right) \right)^2$$
$$+ \frac{1}{2} \sum_{j,a} d''_{ja} \left( \left| r_{ja} - r_a(\phi)^2 c^K(\phi) \right| \right)^2$$  \hspace{1cm} (3.5.16)$$

for the four covalent bonds. Equation (3.5.16) is a correction to reference [58]. The bond strength terms $d'_{ij}$ and $d''_{ij}$ are modified to reduce quickly to zero for faces that are well distorted, by

$$d^K_{ja} = d^K_{ja} f\left( 2r_{ja} / r_{ij}, \theta^K(\phi), \theta^K_a(\phi) \right)$$  \hspace{1cm} (3.5.17)$$

where $^*$ is either $'$ or $''$. As the optimum bond angle in equation (3.5.16) interpolates between tetrahedral and hexagonal structures, $V_K$ cannot correctly model sp hybridised atoms. To prevent large penalties for 180° bond angles in such cases, Heggie suggests omitting $V_K$ if two or less bonds have $d''_{ij} > 0.6$ eV. This, however, introduces a discontinuity into the potential.

The stacking repulsive term takes effect as the Morse-like repulsive term is cut off. It is given by

$$\left( V_{tr}^s \right)_j = f\left( r_{0}, r_{1}, r_{a} \right) \left[ \left( 4s_1 / r_{ij}^2 \right) f\left( q_{ij}, q_i, q_a \right) + s_2 f\left( q_{ij}, q'_i, q'_a \right) \right]$$  \hspace{1cm} (3.5.18)$$

where

$$q_{ij} = \begin{cases} \sqrt{r_{0}^2 \left( p''_{0} - \frac{1}{2} \right)^4} & p'' > \frac{1}{2} \\ 0 & p'' < \frac{1}{2} \end{cases} \text{ and } p'' = \sqrt{\left( 1 - \left| p_{ij} \right|^2 \right) \left( 1 - \left| p'_i \right|^2 \right)}$$  \hspace{1cm} (3.5.19)$$
The repulsion is due to the interaction of the p orbitals on different atoms, so the term only has an effect when the \( p \) and \( p_j \) vectors have a large magnitude and a direction close to that of the internuclear vector. Equation (3.5.18) contains two corrections to reference [58].

The attractive stacking term acts between \( \pi \) systems in different layers of the graphite structure and is weakened if the hybridisation of the atom is greater than sp\(^2\). The interaction is linear in the interlayer separation and is given by

\[
(V_{\sigma}')_{ij} = \frac{1}{2} s_i r_i \phi_i f\left(2r_{ij}/r_i, \theta_i(\phi_i, \theta_u(\phi_j))\right) \left(\Delta_{ij} + \Delta_{z_2} - c/2\right)
\]  

(3.5.20)

This is sufficient for most calculations, but is not applicable for large expansions between layers, or for calculating surface energies. As the attraction is assumed to come from the interaction of the p orbitals on the covalently bonded atoms, only the three bonds \( iA, iB \) and \( iC \) are considered, so

\[
V_{\sigma} = (V_{\sigma}')_{iA} + (V_{\sigma}')_{iB} + (V_{\sigma}')_{iC}
\]  

(3.5.21)

### 3.5.3 Geometric Parameter Calculation

Three geometric parameters, \( r_{\sigma_j}, \Delta_{ij} \) and \( \Delta_{z_2} \), are required for each face of the proximity cell of an atom, where each face represents a bond. The amount of screening between atoms \( i \) and \( j \) due to electrons on other atoms is measured by \( r_{\sigma_0} \). The elongation of the face in the direction of the unhybridised p orbital of the atom is measured by \( \Delta_{ij} \) and \( \Delta_{z_2} \).

In the following descriptions, only one face is considered and the subscript \( ij \) is dropped for clarity. For an arbitrary edge \( k \), of length \( a_k \), \( b_k \) is the perpendicular distance from the edge to the internuclear intercept \( o \), as shown in figure 3.6.

The parameter \( r_{\sigma} \) is based on the maximum radius of a circle that can be inscribed on the face with its centre at the internuclear intercept, i.e. \( b_m \), were \( b_m = \min(b_k) \). To prevent the potential becoming chaotic when several \( b_k \) are close to \( b_m \), a weighted combination given by

\[
\omega_k = a_k \exp\left[-\alpha(b_k - b_m)^2\right]/[1 + \varepsilon/a_k^2]
\]

\[
r_{\sigma} = \left(\sum \omega_k \right)^{1/\sum \omega_k / b_k}
\]  

(3.5.22)
is used, with a low value for $\varepsilon$ and large value for $\alpha$. This suppresses the effect of edges that are very short or have $b_k$ much greater than $b_m$, and results in a well behaved value for $r_\alpha$ that is close to $b_m$.

![Diagram](image)

**Figure 3.6.** The method of calculating the parameters $r_\varepsilon$, $\Delta_1$ and $\Delta_2$ for one face of a proximity cell.

The parameters $\Delta_1$ and $\Delta_2$ are used to simulate geometrical limits on $\pi$ bonding. They are based on the distance from the internuclear intercept to edges of the face, along the direction of $p_\parallel$ (the projection of $p_\parallel$ onto the face). The measure of elongation is reduced if $p_\parallel'$ does not intersect perpendicular to the edge. For the two intersected edges, the parameters are given by

$$
\Delta_1 = r_k' + \max(\delta_k) \quad \text{and} \quad \Delta_2 = r_k' + \min(\delta_k)
$$

(3.5.23)

where $\delta_k$ is the distance along $p_k'$ from the internuclear intercept to the centre of a tangent circle, radius $r_k'$, of edge $k$. Equation (3.5.23) is a correction to reference [58]. The radius of the circle is taken as

$$
r_k' = \frac{1}{4} r_{\varepsilon} [3 - 2 \max(\beta_k, \frac{1}{2})]
$$

(3.5.24)

where $\beta_k$ is the angle between the edge and the projection as defined in figure 3.6.
3.5.4 Obtaining the $p_i$ Vectors

As stated in section 3.5.2, the vectors representing the $p$ orbitals on the carbon atoms are not defined within the potential. Heggie suggests choosing an initial guess for each vector and optimising all vectors, with the total energy of the system as the objective function. This method should give the most reliable predictions from the potential, and is sufficiently fast to use in static calculations such as those for defect energies. There are some drawbacks to this method for using the potential for dynamic calculations. Due to the number of force calculations that are required, the optimisation algorithm must converge rapidly to a value for the $p_i$ vectors. The energy surface with respect to the $p_i$ will typically have many local minima, so finding the optimum global value for all vectors is extremely difficult, if not impossible.

The aim of implementing the potential was to enable direct comparison with the Tersoff type potential's description of graphite, i.e. full MD calculations with a system of over 1000 atoms for a run time of around 1 ps (5000 steps of 0.2 fs). The calculation of forces at each timestep requires the re-evaluation of the energy of each atom and its neighbours six times. Any global optimisation algorithm would therefore greatly increase the computational resources required to conduct the simulation. A more rapid, but approximate optimisation algorithm could have been used, but this was ruled as chaotic behaviour could be introduced into the simulation by local minima being found. Instead it was chosen to calculate an estimate of the direction and magnitude of the $p_i$ vector based on the local geometry of each atom.

The magnitude of $p_i$ is given by

$$
|p_i| = \begin{cases} 
0, & N_i \geq 4 \\
4 - N_i, & 3 < N_i < 4 \\
1, & 2 < N_i \leq 3 \\
N_i - 1, & 1 < N_i \leq 2 \\
0, & N_i \leq 1 
\end{cases} 
$$

(3.5.25)

where

$$
N_i = \sum_j f_e(r_{ij})
$$

(3.5.26)

gives the number of near neighbours of atom $i$ and
\[ f_c(r) = 1 - f(r, 1.694 \text{ Å}, 2.214 \text{ Å}) \]  
(3.5.27)

is a smooth cutoff function. The values for the cutoff are 110% of the diamond nearest neighbour distance and 90% of the graphite second neighbour distance. The magnitude is required to be zero when there is only one neighbour, as there is insufficient information to calculate a direction for the vector. This is of little consequence, as the potential is only expected to model sp² and sp³ hybridised atoms.

If \(|p|\) is non-zero, the direction of the vector is defined in the following manner. For two neighbours within the cutoff of 2.214 Å, the direction is given as the normal to the plane containing \(i\) and the two neighbours. If there are three or more neighbours within the cutoff, the direction is given by the plane passing through the nearest three neighbours. The direction is well defined, but it must be noted that this approximate method introduces a discontinuity when the three atoms defining the plane change due to movement in the cutoff region. However, no reliable method has been found to calculate the direction as a continuously varying function of the local geometry of the atom. The same problems occur when generating the vector by an optimisation method, as slight changes in the local environment produce sudden jumps in the direction, and discontinuities in the potential will arise as local minima are sometimes found. It is noted that this is not the only discontinuity in the potential, as a discontinuity is associated with the Keating term given in equation (3.5.16) in order to allow the approximate modelling of sp hybridised atoms. The inaccuracy caused by the very occasional jumps in the direction is small compared to that introduced by the necessity to use numerical differentiation to generate the forces on atoms. Hence, although the method is far from ideal, it has been applied in the simulations using the potential presented in this thesis.

3.5.5 Generation of the Proximity Cells

Before the potential can be calculated, the proximity cell for the atom concerned must be constructed. From the definition of the proximity cell, the faces of the cell lie in planes normal to and bisecting the internuclear vectors with neighbouring atoms. It is a simple matter to write an algorithm that will usually produce the desired cell for a random configuration of atoms by constructing all possible faces and vertices and testing which ones can ‘see’ the centre atom, e.g. see references [56, 142]. This algorithm will normally produce the desired cell, but may fail if degenerate faces occur. For example the algorithm must be able to deal
with a possible face that doesn't form part of the cell, but has vertices that are on the cell boundary. Another possible problem is the intersection of more than three planes at a point, i.e. an apex with a hedral valency greater than three. There are two variants of the proximity cell for bulk graphite; the first type of degeneracy occurs nine times in the construction of either cell and one variant has two apices with a hedral valency of six.

Figure 3.7. View normal to the graphite plane showing the proximity cell for one atom. The grey lines indicate degenerate faces.

Figure 3.8. Proximity cells for diamond and graphite.

In addition to this, the proximity cells constructed for atoms at surfaces of lattices and molecules will have some infinite faces and an infinite volume. A more sophisticated algorithm for the cell construction was chosen [143]. To simplify the procedure and reduce the number of calculations required the 'supra-polyhedron' is created. This is the polyhedron with faces passing through the
neighbouring atoms, i.e. it is twice the size of the proximity cell. An initial imaginary tetrahedron is defined that has the object atom at its centre and is so large as to always be outside the supra-polyhedron. The neighbouring atoms are sorted by distance from the object atom. Starting with the closest atom, the plane normal to the internuclear vector and passing through the atom is defined. All vertices of the existing polyhedron are checked to see if they lie outside of this plane. If any do, they are removed and a new face and apices are created in the lopping plane; old faces and apices are modified. All neighbour atoms are checked in order until no more vertices can be removed. The polyhedron is then scaled to the correct size. If the true proximity cell of the atom is infinite, the cell produced by this algorithm contains some of the faces of the imaginary tetrahedron. Facets that should be infinite will be very large. The imaginary facets can be safely ignored by the potential, but the extremely large facets due to surfaces must be treated specially to get physically meaningful results.

3.5.6 Modifications to the Potential to Allow for Surfaces

As noted in section 3.5.1, the potential was not designed to model surfaces or large interlayer separations in graphite. However, the envisaged simulations required a graphite surface. To enable this to be carried out, a modification has been made to the potential. The functions \( \langle V_r \rangle, \langle V'_r \rangle, d, \) and \( V_k \) all decrease with increasing bond length, but terms involving interlayer separation are unbounded. The interlayer attractive term is linear in separation and the term coupling interlayer separation and in-plane bonding is quadratic in separation. The term for \( \phi' \) in equation (3.5.12) has a maximum at \( \Delta_1 = \Delta_2 = c/4 - s_1/2s_2 = 2.137 \text{ Å} \). This corresponds to an interlayer separation of 4.275 Å and so provides a convenient distance at which to limit interactions. This limiting is achieved by modifying the values of the geometric parameters calculated from the proximity cell. \( \Delta_1, \Delta_2 \) and \( r_\sigma \) are all constrained to be less than 2.137 Å (by definition \( r_\sigma \) must be less than or equal to \( \Delta_1 \) and \( \Delta_2 \)). This also overcomes the problem of calculating the geometric parameters for surface atoms, which have proximity cells with unbounded faces as described in section 3.5.5. This fix stabilises surfaces, but surface energies have not been fit and are not well described.
3.5.7 Force Calculation

As the potential relies on geometric quantities such as the area of faces of the proximity cell, it cannot be analytically differentiated. The potential must be numerically differentiated with respect to the position each atom in the system at every timestep. This is computationally expensive and is less accurate than analytical differentiation.

To get the force on an atom, the change in potential energy of the system is found as the atom is perturbed from its true position. Using central differences in three dimensions requires six evaluations of the total potential for every atom at each timestep. Due to the formulation of the potential, the movement of an atom will affect the potential energy of atoms directly, or secondarily bonded to it. This means that the potential energy of around thirty atoms must be evaluated for each perturbation to obtain the force on one atom. The need to use numerical differentiation, coupled with the increased complexity of this potential has a dramatic effect on the runtime of a simulation. A trajectory that would take twelve hours to simulate with Tersoff's potential will take three weeks with Heggie's potential. For this reason the potential is only used in cases where the accuracy of Tersoff-type potentials is in doubt.
3.6 Potential Functions for High Energy Interactions

For simulations where high energy collisions occur, screened Coulomb potentials [123] have been used to describe interactions. There are two situations where these potentials are required. The interactions of noble gas ions used to bombard a target can be modelled by such potentials as they are purely repulsive. As mentioned in section 3.3.3, the repulsive term in Tersoff-type potentials is not sufficiently strong. To remove this deficiency, the repulsive term is usually splined to a screened Coulomb potential for interactions within some specified, short distance. For the work presented in this thesis, the ZBL 'universal' potential [144] has been used to model the interactions of noble gas ions, whilst the Molière potential [145] was used to model the close-range repulsive parts of the Tersoff potential.

A general screened Coulomb potential between two atoms is given by

\[
V(r) = \frac{C}{r} \Phi(r/a)
\]

\[
C = \frac{Z_i Z_j e^2}{a 4 \pi \varepsilon_0}
\]

\[
\Phi(r/a) = \sum_{i=1}^{n} c_i \exp[-d_i r/a]
\]

\[
\frac{e^2}{4 \pi \varepsilon_0} = 14.3997 \text{ eVÅ}
\]

where \(a\) is the screening length, \(Z_i\) is the atomic number of atom \(i\), \(e\) is the charge on an electron and \(\varepsilon_0\) is the permittivity of vacuum. The values of the constants \(c_i\) and \(d_i\) and the expression for the screening length are different for the various potentials. The screening lengths used within the two potentials are given in equation (3.6.2), where \(a_b\) is the Bohr radius. The screening length used with the universal potential is that developed by Ziegler, Biersack & Littmark, whilst a length of 0.83 times the Firsov value is used with the Molière potential [69].

\[
\text{ZBL 'universal'} \quad a = \left(\frac{9 \pi^2}{128}\right)^{1/3} a_b \left(Z_1^{0.23} + Z_2^{0.23}\right)^{-1}
\]

\[
\text{Molière} \quad a = 0.83 \left(\frac{9 \pi^2}{128}\right)^{1/3} a_b \left(Z_1^{0.5} + Z_2^{0.5}\right)^{-2/3}
\]

\[a_b = 0.5292 \text{ Å}\]
The constants $c$ and $d_i$ for these two potentials are given in table 3.9. Those used with the 'universal' potential are derived from a rms average of data from about 500 ion-target combinations, whilst Molière produced his parameters as an analytic approximation to the Thomas-Fermi potential.

<table>
<thead>
<tr>
<th>$i$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_i$</td>
<td>0.028171</td>
<td>0.28022</td>
<td>0.50986</td>
<td>0.18175</td>
</tr>
<tr>
<td>$d_i$</td>
<td>0.20162</td>
<td>0.40290</td>
<td>0.94229</td>
<td>3.1998</td>
</tr>
<tr>
<td>Molière</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c_i$</td>
<td>0.35</td>
<td>0.55</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>$d_i$</td>
<td>0.3</td>
<td>1.2</td>
<td>6.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.9. The constants used in the ZBL and Molière potentials.

To make the potential short ranged for noble gas interactions, it is smoothly truncated by the usual cosine cutoff function at distances between 90% and 110% of the sum of the radii of the atoms involved. The parameters used for argon bombardment are given in table 3.10.

<table>
<thead>
<tr>
<th>$R^{(1)}$</th>
<th>C-Ar</th>
<th>Si-Ar</th>
<th>H-Ar</th>
<th>Ar-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.3850</td>
<td>2.7481</td>
<td>1.9597</td>
<td>3.3795</td>
</tr>
<tr>
<td>$R^{(2)}$</td>
<td>2.9150</td>
<td>3.3589</td>
<td>2.3953</td>
<td>4.1305</td>
</tr>
</tbody>
</table>

Table 3.10. Cutoff parameters for argon interactions.

When the screened Coulomb potential is used in conjunction with the repulsive part of the Tersoff potential, it is only used for atomic separations less than some specified value $r_a$. The repulsive part of the Tersoff potential is used for separations greater than a value $r_b$, and the two functions are smoothly joined by a 'spline' function. The chosen spline function is an exponential and has the form $V_{R}^{\text{spline}}(r) = c + \exp(ar + b)$. Using an exponential function, rather than a cubic spline ensures that the energy and force increase monotonically throughout the spline region. The repulsive potential is then given by

$$V_R(r) = \begin{cases} V_{R}^{\text{Molière}} + s, & r < r_a \\ c + \exp(ar + b), & r_a < r < r_b \\ V_{R}^{\text{Tersoff}}, & r > r_b \end{cases}$$  \hspace{1cm} (3.6.3)
The values of the parameters $a$ and $b$ are obtained by fitting to the derivatives of the Tersoff and Molière functions at $r_a$ and $r_b$. The values of $c$ and $s$ are then specified to ensure that the potential is continuous at $r_a$ and $r_b$. The values of $r_a$ and $r_b$ are adjusted so that the shifting of the screened Coulomb potential is approximately equal to the contribution of the many-body attractive part of the Tersoff-type potential at $r_a$, and so that there are not large discontinuities in the second derivative at these points. The parameters used for the spline functions for Tersoff's Si/C potential are given in table 3.11.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$r_a$ (Å)</th>
<th>$r_b$ (Å)</th>
<th>$a$ (Å$^{-1}$)</th>
<th>$b$</th>
<th>$c$ (eV)</th>
<th>$s$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Si</td>
<td>0.286968</td>
<td>0.652200</td>
<td>-7.15522</td>
<td>9.50213</td>
<td>237.359</td>
<td>296.827</td>
</tr>
<tr>
<td>Si-C</td>
<td>0.286968</td>
<td>0.652200</td>
<td>-5.90430</td>
<td>8.59831</td>
<td>112.845</td>
<td>292.680</td>
</tr>
<tr>
<td>C-C</td>
<td>0.286968</td>
<td>0.369580</td>
<td>-9.19618</td>
<td>8.37982</td>
<td>238.344</td>
<td>138.583</td>
</tr>
</tbody>
</table>

Table 3.11. Parameters for the spline functions for use with Tersoff's Si/C potential.

3.7 Long Range Potential Functions

3.7.1 Introduction

Although the short-ranged potentials used in this thesis describe the interactions between atoms within crystals and small molecules, they do not describe non-bonded interactions between atoms and molecules. As these long-ranged interactions are weak compared to short-ranged interactions, their omission from the model usually has very little effect. There are, however, some situations where long-ranged forces contribute to, or dominate the interactions that determine the behaviour of the systems. For example the structure of graphite, fullerite and hydrocarbon crystals are determined by non-bonded interactions. For this reason, it is sometimes necessary to add descriptions of long-ranged interactions to the model of the system being simulated.

3.7.2 Adding Non-Bonded Interactions to Short-Ranged Potentials

To describe the interlayer forces in graphite and similar interactions in fullerite (solid $C_{60}$) crystals and polyethylene, long-range pairwise potentials may be added to simulations using Tersoff or other short ranged potentials. Whilst potentials to describe nonbonded interactions are incorporated into MD studies of polymers [146-148] and have been previously used with the Brenner potential.
[126,149], they have severe limitations. These methods require the atoms that are to experience long range interactions to be specified at the beginning of the simulation and preclude the possibility of reaction and bonding between molecules. Hence these methods are not suitable for studying large disturbances, where bond breaking and bond formation will occur.

Here, we develop an extension to the usual method of adding pair terms to model non-bonded interactions between atoms in different molecules. An additional cutoff function is introduced to produce a long range potential that stabilises the structure of molecular solids, whilst allowing reactions between molecules. The pairwise additive long range potential is written as

$$V_{ij}^{\text{LR}}(r_{ij}) = F_{ij}^{\text{cov}}V_{ij}^{\text{LR}}(r_{ij})$$

(3.7.1)

The long range interaction between any two atoms is modified by a function dependent upon the connectedness of the atoms via covalent bonds. By using the neighbour lists created whilst calculating short ranged interactions, it is simple to check if the two atoms are connected by covalent bonds. The function $F_{ij}^{\text{cov}}$ cuts out the interaction between $i$ and $j$ if they are connected via three or less bonds.

$$F_{ij}^{\text{cov}} = \begin{cases} 1, & w_{ij} \leq 0 \\ \frac{1}{2} + \frac{1}{2} \cos[nw_{ij}], & 0 < w_{ij} < 1 \\ 0, & w_{ij} \geq 1 \end{cases}$$

(3.7.2)

where

$$w_{ij} = f_{ij}(r_{ij}) + \sum_{k \neq i,j} f_{ik}(r_{ik})f_{jk}(r_{jk}) + \sum_{l \neq i,j,k} f_{il}(r_{il})f_{jl}(r_{jl})f_{kl}(r_{kl})$$

(3.7.3)

and $f_{ij}(r_{ij})$ is the short range cutoff function used in the Tersoff type potential.

A separate neighbour list is used for the long range interactions. Depending upon the atoms involved, the basic form of the long range pair term is either a Lennard-Jones 6-12 potential or a Buckingham potential given by

$$V_{ij}^{\text{LR}}(r_{ij}) = V_{\text{cLJ}} \left[ \left( \frac{r_{eq}}{r_{ij}} \right)^{12} - 2 \left( \frac{r_{eq}}{r_{ij}} \right)^{6} \right]$$

or

$$V_{ij}^{\text{LR}}(r_{ij}) = A_{ij}r_{ij}^{n} + B_{ij} \exp(-C_{ij}r_{ij})$$

(3.7.4)
where \( V \) and \( r \), or \( A, B \) and \( C \) characterise the non-bonded interaction between atoms of type \( i \) and \( j \). The functions in equation (3.7.4) are modified to limit the magnitude of the repulsive part of the function by fitting a quadratic spline for separations at which the potential becomes positive. This spline is fit to the gradient of the basic potential at the point at which it equals zero and is constrained to have zero gradient at the distance at which the short range potential begins to act (around 2 Å, depending upon the potential used). Limiting the repulsive part of the interaction in this way ensures that atoms are not prevented from approaching one another and interacting via the covalent potential. The true nature of the repulsive part of the long range potential will differ from this function, depending upon the local environment of the atoms involved. The best that can be achieved with this approximate pair potential is to model the correct equilibrium behaviour for stable molecules, whilst allowing atoms to react when covalent bonds are broken during high energy simulations. Interactions are smoothly cut off at large separations by

\[
f^{lr}_{ij}(r_{ij}) = \begin{cases} 
    1, & r_{ij} \leq R^{(i)}_{ij} \\
    \frac{1}{2} + \frac{1}{2} \cos \left[ \pi \left( r_{ij} - R^{(i)}_{ij} \right) \right] / \left[ (R^{(i)}_{ij} - R^{(o)}_{ij}) \right], & R^{(i)}_{ij} < r_{ij} < R^{(o)}_{ij} \\
    0, & r_{ij} \geq R^{(o)}_{ij}
\end{cases}
\]  

(3.7.5)

The potential used to model interlayer terms in graphite is shown in figure 3.9. tables 3.12 and 3.13 give parameters used to model different interactions together with the cutoff distances used.

<table>
<thead>
<tr>
<th>Potential</th>
<th>( V ) (eV)</th>
<th>( r ) (eV)</th>
<th>( R^{(i)} ) (Å)</th>
<th>( R^{(o)} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C graphite</td>
<td>0.0037</td>
<td>3.85</td>
<td>5.0</td>
<td>5.5</td>
</tr>
<tr>
<td>C-C fullerite</td>
<td>0.0029</td>
<td>3.89</td>
<td>10.5</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Table 3.12. Parameters for the Lennard-Jones long range potential for carbon (fitted to separation and cohesive energy).

<table>
<thead>
<tr>
<th>Potential</th>
<th>( A ) (eV)</th>
<th>( B ) (eV)</th>
<th>( C ) (Å(^{-1}))</th>
<th>( R^{(i)} ) (Å)</th>
<th>( R^{(o)} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C polyethylene</td>
<td>-24.63</td>
<td>3626.72</td>
<td>3.60</td>
<td>5.5</td>
<td>6.0</td>
</tr>
<tr>
<td>C-H polyethylene</td>
<td>-5.42</td>
<td>380.148</td>
<td>3.67</td>
<td>5.0</td>
<td>5.5</td>
</tr>
<tr>
<td>H-H polyethylene</td>
<td>-1.18</td>
<td>115.904</td>
<td>3.74</td>
<td>4.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 3.13. Parameters for the Buckingham long range potential for polymers (taken from reference [150]).
Fig 3.9. The long range interaction potential between two atoms in graphite, for use in conjunction with Brenner's potential. The quadratic spline is fit to have zero gradient at 2 Å.

Preliminary results obtained using these potentials are very promising, but some problems still remain to be solved. The potentials give the correct cohesive energy and structures for graphite, fullerite and polyethylene. However, the limiting of the repulsive part of the potential to allow reaction between atoms, means that the behaviour of materials under compression is not well described. There is also a problem with the description of interactions between isolated atoms or radicals, as no repulsive term would be expected in such interactions. To overcome these problems, the local environment of the atoms needs to be considered. One possibility is the refitting of the long-range potential, along with the addition of some sort of 'bond order' term to the attractive component of the potential. Unfortunately due to the constraints of time, such work remains to be completed at a later date.

3.7.3 Low Energy Interactions Between Fullerenes

At temperatures above 300 K C60 molecules rotate freely with angular velocities of at around $10^9$ revolutions times per second in the fullerite structure.
As the molecule is approximately spherical, it can be accurately modelled by smoothing out the 60 carbon atoms to produce a shell of uniform density. Girifalco [153] has produced an analytical potential in this manner. The functional form of the potential is obtained by assuming a Lennard-Jones potential between individual carbon atoms and integrating over the surface of two spheres. This gives the potential between two fullerenes whose centres are a distance $r_{ij}$ apart as

$$V^{C_{60}}_{ij}(r_{ij}) = -\alpha \left[ \frac{1}{s(s-1)^5} + \frac{1}{s(s+1)^5} - \frac{2}{s^6} \right] + \beta \left[ \frac{1}{s(s-1)^7} + \frac{1}{s(s+1)^7} - \frac{2}{s^8} \right]$$

where $s = r_{ij}/2a$

and $2a$ is the fullerene diameter of 7.1 Å, $\alpha=4.67761 \times 10^2$ eV and $\beta=8.48573 \times 10^{-5}$ eV.

This potential can be used to model interactions between fullerenes provided the simulation is being conducted at temperatures in excess of 300 K, and the energy of molecules is below the threshold at which reaction can occur between them. This is a great advantage over using pair potentials between individual atoms, as it reduces the number of long-range interactions by a factor of 360. When the potential is used in this thesis, the interaction is smoothly truncated between distances of 24.9 Å and 25.5 Å to further reduce the number of calculations required. This cutoff distance was chosen as it is midway between the second and third neighbour shells in the fcc structure, and the molecular interaction predicted by the Girifalco potential is negligible at third and greater neighbour distances [153].

### 3.7.4 Fullerene Interaction with a Silicon Substrate

To enable simulations of fullerene film growth to be conducted, a potential was required to model the interaction between the first layer of the fullerene film and the substrate. The interaction between the undercoordinated surface atoms on the {100}(2×1) or {111}(7×7) silicon surfaces and the fullerene involves charge transfer from the substrate to the molecule [154,155], and is not modelled by Tersoff-type covalent potentials. Pair potentials between individual C and Si atoms were attempted, but none could be found that predicted the correct orientation of the fullerene and the correct binding site on the dimer reconstructed surface. Instead, a Lennard-Jones function smoothly truncated at 1.5 times the equilibrium distance is used to model the interaction between the molecule and
individual surface silicon atoms. As this function treats the fullerene as a single object, it does not prevent the rotation of the molecule on the surface. The parameters of the potential are given in Table 3.14, they were fit to reproduce the nearest neighbour distance of 7.2 Å and to prevent desorption of molecules from the surface at temperatures up to 1000 K as reported by Wang et al. [45,46]. The potential correctly predicts the favoured binding site to be at the centre of four dimer pairs on the \( \{100\}\) surface.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Potential} & V_{e} (\text{eV}) & r_{e} (\text{Å}) & R^{(0)} (\text{Å}) & R^{(0)} (\text{Å}) \\
\hline
C_{60}-\text{Si} & 0.34 & 7.99 & 10.3 & 10.8 \\
\hline
\end{array}
\]

Table 3.14. Parameters for the fullerene-silicon substrate interaction potential.

3.7.5 Timing Considerations When Using Long-Ranged Potentials

A drawback of applying long-range interactions to a simulation is the number of neighbours that must be considered for each atom. With a short-ranged potential, each atom will typically interact with only three or four others. The cutoff distance for long range interactions is typically between 5 Å and 10 Å, compared with around 2 Å for short ranged interactions. This in consequence leads to a long range neighbour list containing between 50 and 450 atoms. The functional form outlined in section 3.7.1 will prevent most of these interactions being considered, so the calculation of the pair term is not an important factor in the time of the calculation. The main cost is the time and memory required to store and retrieve the neighbour information, plus the processing necessary to check the connectivity of atoms. For these reasons, long ranged interactions cannot be added as a matter of course, but are used only when they are expected to be critical to the accuracy of the simulation. A possible method of reducing the size of the long-range neighbour lists would be to only store neighbours for which function \( F^{\text{cov}} \), defined in equation (3.7.2) is non-zero. As \( F^{\text{cov}} \) depends upon the short-range cutoff function, it would then be necessary to update the long-range neighbour lists of all bonded neighbours of an atom, if that atom's local environment (i.e. short range interactions) changed.
3.8 Testing and Modification of Potential Functions

3.8.1 Introduction

Although the semi-empirical potentials described in sections 3.5 and 3.6 are fitted to a selection of properties, both for bulk material and small molecules, they are usually applied in simulations where configurations arise that are far from those fitted. For example, none of the carbon potentials was explicitly fitted to reproduce properties of the C\textsubscript{60} molecule. There are plenty of examples in the literature of calculations leading to unphysical predictions due to the application of empirical potentials where they were not valid (see for example references [156,157]). It is therefore necessary to thoroughly examine the possible potential functions before starting any new simulation work. Examples are given in sections 3.8.2 and 3.8.3 that illustrate the testing and modification of potentials that may be required to obtain good results when using empirical potentials.

The predictions of the potentials are compared with experimental data when it is available, and with the results of ab-initio calculations. By examining several potentials, a potential function that gives a good description of the phenomena being studied can usually be found. The best function available may still have deficiencies and require modification to more accurately reproduce known data.

3.8.2 The Selection of a Potential Function to Model C\textsubscript{60}

Before beginning simulations to study the interaction of C\textsubscript{60} with isolated atoms or crystal surfaces, the descriptions of C\textsubscript{60} given by the available potential functions were examined. The proximity cell potential gives a stable structure for the fullerene, but the description is unsatisfactory due to the potential’s inability to accurately model surfaces. Table 3.15 gives a comparison of the minimum energy structure of C\textsubscript{60} predicted by the Tersoff [101] and Brenner [65] potentials. All the potentials give a stable C\textsubscript{60} structure and it can be seen that the first parameterisation of the Brenner potential (Brenner 1) gives the best agreement with the reported calculations and experimental measurements for the size and structure of the C\textsubscript{60} cage. Hence the first parameterisation of Brenner’s potential is usually chosen for simulations where the primary aim is to investigate the behaviour of fullerenes.
Table 3.15. Calculated radii, bond lengths and potential energy of the C\textsubscript{60} structure for different empirical potentials. The radius refers to the distance of the C atoms from their centre of mass.

*Deduced from the heats of formation given in [159].
†Calculated from the values given for bond lengths.

3.8.3 Comparison of the Description of C\textsubscript{60} Collision with a Graphite Surface

As a method of comparing the suitability of different potentials for describing interactions of fullerenes, the collision of C\textsubscript{60} with a graphite surface was examined using various empirical functions. Experiments to determine the products from collisions of charged fullerene molecules with graphite [29-32] revealed no fragmentation of the fullerenes at incident energies below 250 eV. Simulations conducted by Smith & Webb [16] have determined the main features of such interactions. They found that the fullerene was reflected intact at normal incidence with energies up to 250 eV, and a depression wave spread radially from the point of impact. This wave was preceded by fronts that had a velocity approximately ten times greater than that of the depression, but transported very little energy across the surface. Computer visualisation showed that the structure of ripples on the surface was relatively independent of bombardment energy between 50 eV and 1 keV.

Three potential functions are compared here, namely Tersoff’s potential [101], the first parameterisation of Brenner’s potential [65], and Heggie’s potential [58]. Heggie’s potential is the only one that models the interlayer forces that occur between separate graphite planes. It has the disadvantage that it is at least an order of magnitude slower to evaluate than the Tersoff type potentials, due to the reasons given in section 3.5. In the simulations described below, a fullerene with a kinetic energy of 500 eV is normally incident on the surface of graphite (0001). Experimental results for C\textsubscript{60} impact on various surfaces indicate that this is slightly above the threshold where damage may occur to the fullerene. The molecule would be expected to remain mostly intact, with some bond
breaking and the possibility of reaction with the graphite surface. Only a small
amount of damage should occur to the graphite surface in the vicinity of the
impact point, but considerable distortion of the surface graphite planes is
expected.

Figure 3.10(a) shows atomic positions during the initial 0.8 ps of a 500 eV
fullerene impact with a graphite surface, modelled using Tersoff's potential. The
target was dimensioned 76 Å × 76 Å, giving 2205 atoms per layer and was
5 layers deep. The system was initially at zero K, and free boundary conditions
were applied to the sides of the target. A sufficiently large target was used so that
the simulation could be run for around 1.0 ps before motion occurred at the edge
of the simulated region. The features of the simulation are consistent with those of
reference [16]. The impact produces a travelling depression wave with a raised
distance, the shape of the wave is hexagonal rather than circular, reflecting
the structure of the graphite surface. The peak of the wavefront travels a distance of
35.3 Å in 0.8 ps, an average velocity of 4414 ms⁻¹. The motion of the top layer
towards the second layer causes the atoms in the two layers to come within
interaction distance (2.1 Å) after a movement of 1.25 Å. The top layer is reflected
and a plateau begins to form around the impact point after 600 fs. The plateau
spreads from the impact point and has a height approximately equal to that of the
initial height of the surface. The impact energy is sufficiently high to break bonds
within the fullerene, but the molecule remains basically intact. A small amount of
damage occurs to the graphite surface directly at the impact point and several
bonds are formed between the molecule and the surface.

Figure 3.10(b) shows atomic positions during a simulation with identical
initial conditions to that described above, but modelled using Brenner's potential.
The basic features of the simulation are similar to those described for the case
using Tersoff's potential. The different elastic properties of the potential results in
steeper edges to the wave front and a slightly slower wave speed. The peak of the
wavefront travels a distance of 32.2 Å in 0.8 ps, an average velocity of 4031 ms⁻¹.
As with the Tersoff potential, reflection of the top layer from the second leads to
the formation of a plateau around the impact point at approximately the initial
height of the surface. At 0.8 ps, the surface area of the plateau is similar to that
given by the Tersoff potential, but the plateau is flatter and has steeper sides.
Several bonds are broken within the fullerene, but no atoms are lost from the
molecule. The molecule remains above the graphite surface and several bonds are
formed between the fullerene and the graphite surface.
Figure 3.10. Atomic positions during 500 eV $C_{60}$ normal incidence on graphite using (a) Tersoff's potential and (b) Brenner's potential.
Simulations were also conducted using Heggie's proximity cell potential to model interactions. The modifications proposed in section 3.5.6 were applied to the geometric parameter calculation in order to enable a graphite surface and fullerene to be modelled whilst retaining the interlayer terms. Figure 3.11(a) shows atomic positions during the initial 0.3 ps of a 500 eV fullerene impact with a graphite surface initially at zero K. The target was dimensioned 41 Å x 41 Å, giving 640 atoms per layer and was 4 layers deep. It was necessary to simulate a smaller system compared to the simulations conducted with the Tersoff and Brenner potentials described above, due to the computational expense of evaluating the potential and forces. Free boundary conditions were again applied to the sides of the target. Due to the long-ranged nature of the potential it was necessary to start the simulation with the fullerene some 11.5 Å above the surface of the graphite, compared to a distance of 5.5 Å used with short ranged Tersoff-type potentials. Thus a considerable time is spent calculating the fullerene's motion towards the surface, with very little interaction. The initial features of the interaction are similar to those described by the Tersoff-type potentials, although the simulation time is too short to allow a full comparison (the results presented here required a weeks computing on a HP 735 workstation). The impact produces a hexagonal depression wave with a raised edge and the molecule remains intact. Figure 3.11(b.i) shows the hexagonal deformation of the graphite surface during a 250 eV interaction. This can be compared to figure 3.11(b.ii), which shows the prediction of the Tersoff potential at 266 fs. The stability of the fullerene and the deformation of the surface are clearly visible. The deficiency of the Heggie potential in describing graphite layers can be seen, as a puckered surface is formed.

The most striking difference between the simulation results occurs at the edges of the simulated region. As free boundaries are used, the edges of the graphite planes are covered with dangling bonds. Simulations using Tersoff type potentials lead to a small amount of relaxation from the bulk graphite structure, but the layers remain planar. The planar configuration also appears to be a metastable state with respect to the Heggie potential, but reconstruction occurs as soon as the edge atoms gain any velocity perpendicular to the planes. This is illustrated in figure 3.11(c) for the case of a system of two graphite planes with free boundary conditions applied. The two edges are attracted towards each other as the dangling bonds on the edges are saturated by the formation of new covalent bonds. The atoms in the region of the edge are sp² hybridised, but the graphite contains defects and five, six and seven membered rings are formed.
Figure 3.11 (a) Atomic positions during 500 eV $\text{C}_{60}$ normal incidence on graphite. (b) Comparison of Tersoff and Heggie potentials. (c) Predicted reconstruction at the edges of graphite planes.
These qualitative comparisons of the three carbon potentials show general agreement between the models. The features observed during 500 eV interactions may be summarised in the following manner. The initial impact creates a travelling depression wave with a velocity of approximately $4 \times 10^3$ ms$^{-1}$. The wave has a raised leading edge and a hexagonal structure, and much of the energy is carried away from the impact site by this wave. The velocity of atoms perpendicular to the plane is relatively low and interaction between planes as they approach each other causes repulsion and the direction of motion of the top layer is reversed. Due to the lack of long-range forces in the Tersoff model, there is no constraint on the interlayer separation, except that the atoms in adjacent layers must be out of interaction range (2.1 Å using Tersoff’s potential and 2.0 Å using Brenner’s potential). However, the minimum energy structure for both potentials is a planar graphite structure. The strain caused by deformation from the planar structure is sufficient to cause the sheets to regain some of their original shape. There is no constraint on the actual separation of the layers, but as the mass of the individual graphite layers is large compared to the mass of the fullerene, the inertia of the plane will prevent large movements in the timescales simulated.

The simulations using Heggie’s potential show no qualitative differences in the behaviour of graphite during C$_{60}$ impact. The effect of including a description of the interlayer forces is small as the interactions are very weak compared to the in-plane bonding. It appears to be the strain caused by deformation of the graphite sheet that dominates the motion of atoms during the energetic part of a trajectory. The only major difference observed is the reconstruction at edges of the graphite sheet if free boundary conditions are used. At present the Heggie potential is too expensive to evaluate to allow its routine use in simulation studies. It also has some undesirable properties for a potential for MD simulation as mentioned in section 3.5, so its use in this thesis is avoided if it is possible to use a Tersoff-type potential.

### 3.8.4 Making Modifications to a Potential Function

The way the fullerene interacts with other atoms and molecules is also critical to the outcome and predictions of simulations. Figure 3.10 shows the change in the calculated minimum energy of a system composed of a fullerene and one atom, as the atom approaches an atom in the C$_{60}$ cage. The results of the calculation using three different potential functions for carbon are compared. The potentials used are Tersoff’s Si/C potential [102], and the two parameterisations of Brenner’s C/H potential [65]. The case labelled ‘Si Brenner1’ is the C/Si/H
potential detailed in section 3.4.6, but with the original parameters used for the spline function $F_{cc}$.

![Graph showing interaction energy vs. distance from fullerene](image)

**Figure 3.10.** Change in the minimum energy of a $C_{60}$-single atom system as the atom approaches the fullerene along a line through the fullerene centre of mass and one atom of the cage.

Figure 3.10 shows two related problems with the potential functions. The energy change predicted as a silicon or carbon atom binds to the $C_{60}$ cage using Tersoff’s potential to describe the fullerene is more than twice that when using Brenner’s potential. *Ab-initio* calculations using a local spin-density functional pseudopotential method [160] predict the binding energy for silicon to lie about halfway between the two values as shown in table 3.16. Hence neither of the potentials could be expected to accurately model the interaction of fullerenes with isolated Si atoms. The binding energy for an endohedral hydrogen atom is also underestimated by both parameterisations of Brenner’s potential. The large value of the binding energy calculated with the Tersoff potential is not surprising as this potential gives a relatively poor description of $C_{60}$. The atomisation energy of $C_{60}$ is underestimated by around 10.5 eV, resulting in greater reactivity. This in conjunction with the overbinding of radicals mentioned in section 3.3.3 leads to the large energy gain on bond formation.

The second problem only occurs with Brenner’s potential. The potential gives an energy barrier to the reaction of the $C_{60}$ with either Si or H and spurious ripples in the calculated energy path as a carbon atom approaches the fullerene.
These features have been found to be artifacts of the spline function $F(n_{ij}, n_{ij_{\text{con}}}, n_{ij_{\text{out}}})$, that is used within the potential to model the effect of conjugation of carbon-carbon bonds and to correct for an overbinding of radicals that would otherwise be predicted. As the isolated atom approaches the fullerene, this function weakens the three C-C bonds on the cage atom. The spline function is dependent only upon the coordination of atoms involved in the bond, so its value changes rapidly when neighbours are in the cutoff region of the potential. The bond energy increases gradually between the cutoff and the equilibrium distance, so as an atom approaches the fullerene the three C-C bonds are rapidly weakened, then the binding energy increases as the bond is strengthened between the atom and the C$_6$H$_6$. This causes the spurious features, and the weakening of the three bonds within the fullerene is also responsible for the small value of the calculated energy change when the exohedral complex is formed. The parameter of this spline that affects C-C bonds in a conjugated system where the C atoms have coordinations of 3 and 4 was refit in an attempt to remove these spurious features. The value of $F(2,3,2)$ was altered from -0.0465 to -0.0186 and as a consequence, the derivative $\frac{\partial F(n_{ij}, n_{ij_{\text{con}}}, n_{ij_{\text{out}}})}{\partial n_{ij}}$ changes from 0.03775 to 0.0517.

Figure 3.11 shows the results of the calculation with this modified parameterisation, along with the predictions of the original parameterisation and Tersoff's potential. Also marked on the graph are the minimum energy data from ab-initio calculations for Si-C$_6$H$_6$ and H-C$_6$H$_6$. The artifacts have been eliminated and the predicted energies are in much better agreement with the ab-initio values as shown in table 3.16.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Tersoff</th>
<th>Brenner 1</th>
<th>Brenner 2</th>
<th>Brenner M</th>
<th>ab-initio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C$_6$H$_6$</td>
<td>3.59</td>
<td>1.07</td>
<td>1.20</td>
<td>1.84</td>
<td>-</td>
</tr>
<tr>
<td>Si-C$_6$H$_6$</td>
<td>2.47</td>
<td>0.87</td>
<td>-</td>
<td>1.62</td>
<td>1.35‡, 1.84‡</td>
</tr>
<tr>
<td>H-C$_6$H$_6$</td>
<td>-</td>
<td>1.65</td>
<td>1.78</td>
<td>2.40</td>
<td>1.97‡</td>
</tr>
</tbody>
</table>

Table 3.16. Binding energy (eV) calculated for atom-C$_6$H$_6$ systems using empirical and ab-initio calculations. Brenner M is the first parameterisation of Brenner’s potential, with the modified spline function.

† Calculated using a wavefunction basis set of four s and p Gaussian functions with independent exponents (i.e. 16 orbitals) for each atom, with the charge density fitted to Gaussian s-like functions with four independent exponents.
‡ Same as †, but with a larger basis set of eight s and p Gaussian functions (32 orbitals) for the silicon atom.
The original value of $F_{ee}(2,3,2)$ was set equal to that of $F_{ee}(2,3,1)$, which is fit to the vacancy formation energy in diamond. The modification presented above does not affect the description of any structures used for fitting the potential, but will affect many predictions of the potential. The formation energy of multiple vacancies in diamond, the energetics of diamond surfaces, and the description of other diamond-like structures with undercoordinated atoms within a separation of two bonds will be altered. The description of graphite-like structures with one carbon atom fourfold coordinated will also be altered, but the re-fitted potential should give a better description in this area. As the same parameter describes deviations from the diamond structure and deviations from the graphite structure, it is unlikely that a single parameterisation of the potential can be found that accurately describes both situations.

The tweaking of the potential function results in an increase of approximately 0.25 eV in the strength of any C-C bond where one C atom has three neighbours, the other has four and the bond is part of a conjugated system. This modification will have the effect of decreasing the energy of surface carbon atoms. To get an idea of the magnitude of this change, the increase in energy of each affected bond can be assumed to be 0.25 eV. This ignores other factors such as the strain caused by differing bond lengths and angles, but gives a reasonable estimate of the effects. The three bonds on surface atoms of the bulk terminated {111} surface are all affected, so the surface will be more stable by approximately
0.75 eV per surface atom. Each dimer atom on the \{100\}(2\times1) surface has two affected bonds, so the surface will be more stable by around 1.0 eV per dimer. The bulk terminated \{100\} surface is unaffected, leading to an increased energy gain on dimerisation of approximately 6.5 eV per dimer pair. As none of the simulations conducted to date involve a diamond surface or similar structures, the modification of the energetics of such structures is not a great concern. However this spline value is also used in describing many other states. To ensure that this did not seriously affect other predictions of the potential, the molecules used in testing the original parameterisation were examined. The spline term affects one or two bonds, increasing atomisation energies by approximately 0.25 eV and 0.5 eV respectively in eight of these structures. Table 3.17 illustrates the effect of these increases.

<table>
<thead>
<tr>
<th>Affected Molecule</th>
<th>Original Potential</th>
<th>Modified Potential</th>
<th>Experiment</th>
<th>Original Error</th>
<th>New Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopropene</td>
<td>28.2</td>
<td>28.7</td>
<td>28.8</td>
<td>-0.6</td>
<td>-0.1</td>
</tr>
<tr>
<td>cyclobutene</td>
<td>42.4</td>
<td>42.9</td>
<td>42.4</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>cyclopentene</td>
<td>55.7</td>
<td>56.2</td>
<td>55.6</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>1,4-pentadiene</td>
<td>55.0</td>
<td>55.5</td>
<td>54.8</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH} = \text{C} = \text{CH}_2 )</td>
<td>40.4</td>
<td>40.65</td>
<td>42.1</td>
<td>-1.7</td>
<td>-1.45</td>
</tr>
<tr>
<td>toluene</td>
<td>69.6</td>
<td>69.85</td>
<td>70.1</td>
<td>-0.5</td>
<td>-0.25</td>
</tr>
<tr>
<td>1,4-dimethylbenzene</td>
<td>81.8</td>
<td>82.3</td>
<td>82.6</td>
<td>-0.8</td>
<td>-0.3</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>81.9</td>
<td>82.15</td>
<td>82.5</td>
<td>-0.6</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

\[
\frac{1}{n} \sum E_i = -0.4875, \quad -0.0813
\]
\[
\sqrt{\frac{1}{n} \sum E_i^2} = 0.7541, \quad 0.6601
\]

Table 3.17. Estimated effects on atomisation energies (in eV), due to the modification of the spline function for the Brenner 1 potential.

As shown above, the modification results in a reduction in the mean and rms. errors of the calculated values by 83% and 12.4%, respectively. Interestingly, if a constant value is assumed for the increase in bond energy due to the modification, a minimum rms error of 0.6580 eV is obtained at an energy of 0.22 eV per bond. This is very close to the energy obtained by fitting the spline value just to fullerene-atom complexes. The only negative effect of this modification that has been detected is therefore in the alteration of the description of diamond surfaces. With hindsight, it is obvious that the same parameter cannot be expected to accurately describe both diamond surfaces and bonding in small molecules. In
simulations involving diamond surfaces, it may be necessary to use the original value of the parameter or a value between the original and modified values.
Chapter 4

Energetic Fullerene Interactions With Si Crystal Surfaces

4.1 Introduction

The way in which $C_{60}$ molecules interact with crystal surfaces is of interest to surface and materials scientists, and experimental work by a number of groups has shown that fullerenes can be very stable structures in such interactions. For example, Beck et al. [29] have conducted ion beam scattering experiments with fullerenes on $Si\{100\}$. Their results indicated that fullerenes with incident energies up to 200 eV were reflected with no evidence of impact induced fragmentation, but the collisions were highly inelastic. Most of the perpendicular momentum and around 60% of parallel momentum was lost from the fullerene to the silicon lattice, with only about 20% of the kinetic energy retained by the fullerene. In subsequent work, Yeretzian et al. [33] produced a model of the scattering kinematics, based on treating the $C_{60}$ cage as a deformable hollow sphere. Using a harmonic deformation limit of 15 eV calculated using empirical potentials [126], the model quantitatively predicts measured recoil velocities. Busmann et al. [30,31] have performed $C_{60}$ scattering experiments with diamond and graphite surfaces and as a result of these investigations Lill et al. [32] have proposed an energy transfer model. Their proposal is that the molecule remains stable but the tangential component of velocity of the cluster can be partially transformed into rotational energy, with the normal component being transformed into vibrational and deformational energy of the projectile and target.

MD simulations of the interaction of $C_{60}$ with graphite [16] have confirmed these observations and have also shown that rotational motion can be induced by bond interactions between the molecule and the surface. At low energies (less than 250 eV) the molecule remains intact and is usually reflected. Computer visualisation [77] of the interaction process of normally incident $C_{60}$ with a $\{0001\}$ graphite surface showed that a hexagonal wave propagates from the point of impact. Other MD simulations by Mowrey et al. [20] have examined fullerenes normally incident on hydrogen terminated diamond $\{111\}$ with energies between 150 eV and 250 eV. Although the $C_{60}$ cage was severely distorted during these impacts, it remained intact for impact energies up to
150 eV. Higher collision energies led to both reactive and nonreactive scattering and chemsorption. These simulations were carried out for times of the order of approximately 0.5 ps but it was also suggested that fullerenes reflected intact might fragment after a longer time due to their large amount of internal energy.

In the following sections, the interaction of C_{60} with bare and hydrogen terminated silicon surfaces is examined [161,162]. The interaction of C_{60} molecules with bare silicon crystal surfaces is compared to earlier simulations with graphite surfaces [16]. In contrast to the results for graphite, it is found that the molecule rarely reflects intact from the bare silicon surface. Grazing incidence (around 80° to the surface normal) at energies of a few hundred eV results in the fullerene molecule becoming trapped in the surface binding potential. The molecule can roll across the surface for up to one revolution before coming to rest. At normal incidence and energies less than 500 eV the molecule remains intact, but becomes embedded in the surface layers of the silicon lattice. At energies of greater than approximately 500 eV, at grazing incidence, the molecule breaks up on impact with the majority of the carbon atoms reflected. Normal incidence on the bare surface with energies in excess of 1 keV leads to disintegration of the fullerene and sputtering from the crystal. This is especially evident at energies greater than 4 keV where high energy deposition near the impact point creates a crater surrounded by a hot disordered region from which Si atoms can be thermally ejected for times up to the order of 1 ps.

The effects terminating the silicon surface with hydrogen have also been investigated. C_{60} interactions with bare, one monolayer and two monolayer hydrogen terminated Si\{100\} surfaces are compared for molecules with energies from 100 eV to 250 eV. The fullerene can be reflected from the surface, but the C_{60}-surface interaction is strongly affected by the angle of incidence and the structure of the target surface. Energies greater than around 150 eV can cause damage to the fullerene and usually result in the molecule becoming bound to the surface. The fullerene can also be reflected from the surface during the initial impact, but have insufficient momentum to escape from the surface binding potential and undergo further impacts with the surface before coming to rest.

4.2 Comparison of Interactions with Bare Silicon Surfaces

In the work described here, MD simulations were performed of C_{60} interactions with bare Si crystal surfaces. Three different Si surfaces were considered, namely the \{110\} and \{111\} configurations and the dimer reconstructed \{100\}(2×1) surface. The aim of the simulations was to investigate
chemical reactions between the molecule and a bare surface, so no attempt was made to model the oxide passivation layer that is normally present on the silicon surface. As this layer is usually present when surface scattering experiments are conducted, the results of simulation and experiment are not directly comparable. Simulations were conducted with several angles of incidence between normal and grazing, and energies ranging from tens of eV up to 5 keV.

Tersoff's multicomponent potential [102] was used to describe interactions, as it was the only available potential for describing silicon-carbon systems at the time these simulations were conducted. As the potential is not sufficiently repulsive for small separations as mentioned in section 3.3.3, it is splined to a screened Coulomb potential for close particle separation. The splining procedure and precise nature of the screened Coulomb potential is given in detail in section 3.6.

The simulations were carried out using free periodic boundary conditions, rather than enforcing an artificial periodicity on the crystal by applying periodic boundaries. A lattice of sufficient size that edge effects were negligible was used. For the majority of simulations, a lattice dimensioned 84 Å square with a depth of 14 Å was sufficiently large. This gave approximately 6000 atoms in the lattice (9 layers deep with around 650 atoms per layer). For high energy (around 5 keV) interactions, a larger lattice was found to be necessary. The chosen dimensions were 84 Å x 84 Å x 42 Å for normal incidence and 84 Å x 95 Å x 25 Å for 60° incidence. The simulations were started with all atoms at zero K and inelastic energy loss was ignored. Figure 4.1 illustrates the various crystal faces studied, together with the definition of azimuthal angle Φ used in the text.

Two types of simulation were carried out. The first was a detailed investigation of representative trajectories run for long interaction times. For these simulations, a fixed timestep of 0.2 fs was chosen for most simulations. This conserved the total energy of the system to within 1 eV in all the simulations carried out. The second type of simulation was used to determine average sputtering yields at 5 keV, and involved running a small set of representative trajectories. The size of this set was chosen so that the average sputtering yield altered only slightly as further trajectories were run and should be accurate to within 10%. For the sputtering-yield investigation, a slightly less accurate variable timestep algorithm, given in section 2.4.2 was employed to reduce the simulation runtimes.
Figure 4.1. The definition of azimuthal angle $\phi$ used in the text for the various $Si$ crystal faces. The faces are viewed at normal incidence and the atoms are represented by circles whose radii decrease with increasing depth.

The behaviour of silicon under fullerene impact may be contrasted with that of graphite. As shown in section 3.8.3 and reference [16], the weak interlayer forces in graphite mean that its surface deforms easily, while the strong covalent bonds within the layers remain unbroken at energies up to around 500 eV. Due to isotropy of the diamond structure, the strong bonding within the $Si$ crystal prevents the surface deforming so dramatically. Figure 4.2 shows atomic positions during normal incidence of a 50 eV $C_{60}$ molecule on a bulk terminated $Si(111)$ crystal. For clarity in figures 4.2 to 4.9 only a 14 Å thick section of the crystal centred at the impact point with a width of 70 Å and a depth of up to 20 Å is plotted. The direction $\phi=0^\circ$ is left to right across the page.

For 50 eV bombardment, the energy involved is insufficient to break any bonds in either the silicon or the $C_{60}$ molecule. The strong chemical affinity between $C$ and $Si$ causes the fullerene to stick to the silicon surface. In comparison to graphite, silicon is a far harder material and shows much less deformation. The surface ripples caused by the impact are of the order of fractions of 1 Å, compared to heights of the order of 1 Å seen with graphite. After impact, the molecule remains bound to the surface, with all but 4 eV of its initial kinetic energy transferred to the lattice. After 1.25 ps the total potential energy of the system has decreased by 24 eV. This potential energy and the fullerene kinetic energy is conserved by a 70 eV increase in the kinetic energy of atoms around the impact site. At this energy, the molecule remains intact on the $Si$ surface. The
surrounding Si atoms vibrate in their lattice sites with the transferred energy gradually dispersing away from the impact point.

Figure 4.2. The atomic positions for a 50 eV C\textsubscript{60} molecule normally incident on Si\{111\} during a 1.25 ps simulation.

Figure 4.3. The atomic positions for a 100 eV C\textsubscript{60} molecule normally incident on Si\{111\} during a 1.25 ps simulation.
Figures 4.3 and 4.4 compare interactions of a 100 eV $C_{60}$ at $\theta=0^\circ$ with different $Si$ surfaces.

The {111} surface results shown in figure 4.3 can be compared to the more open {110} structure shown in figure 4.4. As would be expected, the $C_{60}$ molecule is able to penetrate deeper into the {110} lattice. Disturbances propagate from the impact point through the lattice structure. After 1 ps, the {111} surface layers almost regain their initial configuration. The {110} surface shows some reformation during the first 500 fs, but there is no any further reformation after 500 fs. Bonds are formed between the carbon and silicon atoms when the fullerene penetrates the {110} surface, these hold the molecule below the crystal surface and prevent the silicon from totally regaining its regular structure. In both cases, the maximum displacement of $Si$ atoms is small, being 3.1 Å and 4.4 Å for the {111} and {110} surfaces respectively after 1.25 ps. The energy changes in these simulations are almost identical with the fullerene retaining 6 eV as vibrational kinetic energy and the majority of kinetic energy (75 eV) being transferred to the surface silicon atoms.

An impact energy of 250 eV on $Si${111} results in a similar interaction, but it can be seen in figure 4.5 that the molecule penetrates the surface and some $Si$ atoms are permanently displaced.
After 1.25 ps the maximum Si atom displacement is approximately 8.5 Å. The atom with the maximum displacement is pushed into the lattice after direct impact from the fullerene. After 1.25 ps, 36 Si atoms have moved a distance of more than half a lattice unit (2.7 Å) from their initial positions. The C$_{60}$ molecule remains intact, and retains a vibrational energy of 15 eV. There are more Si-C bonds formed than at 50 eV incidence energy, but the potential energy of the system is raised by 50 eV due to the damage to the crystal.

When the incident energy of the fullerene is increased to energies in excess of approximately 300 eV, more bonds are broken in the lattice and the molecule becomes implanted in the surface. This is illustrated in figure 4.6, in which C$_{60}$ is normally incident with a kinetic energy of 1 keV. Bonds are broken in both the silicon and the fullerene molecule, creating a dense mixed region around the impact site without any observed sputtering. Approximately 100 atoms are displaced by more than 2.7 Å, with a maximum displacement of 12.2 Å. Most of the displacement of Si atoms is confined to the first 8 layers. Around half the incident energy remains as kinetic energy after 1.25 ps, 90% being transferred to silicon atoms. The potential energy of the atoms involved in collisions is raised significantly as a result of radiation damage, with bonds being broken rather than formed as in the case of the low energy interactions. By comparison with graphite, the silicon lattice is brittle and susceptible to more permanent damage during the
interactions. In graphite at similar energies, the surface waves transfer energy away from the impact position and the strong planar bonds remain unbroken.

Figure 4.6. The atomic positions for a 1 keV C₆₀ molecule normally incident on Si{111} during a 1.25 ps simulation.

Figure 4.7. The atomic positions for a 5 keV C₆₀ molecule normally incident on Si{111} during a 2.0 ps simulation.
Figure 4.7 illustrates the result of \( C_60 \) incident normally at 5 keV on Si\{111\}. The fullerene breaks up on impact, causes sputtering of silicon atoms and forms a large void in the surface. After 2 ps a crater has formed in the surface with a raised rim surrounded by a locally disordered region. The diameter of the crater is about three times that of the \( C_60 \) molecule.

Figures 4.8 and 4.9 show the results of simulations for incidence at \( \theta=60^\circ \). Investigations of the state of the lattice after oblique incidence at an energy of 5 keV show some differences to the normal incidence case. The sputter yield is approximately 50% smaller, and the crater is slightly shallower and is elongated in the direction of motion of the fullerene. For 1 keV incidence, direct knock-on ejection occurs and many of the carbon atoms are reflected, in contrast to normal incidence simulations where no sputtering or reflection occurs. The depth of lattice disorder is only half that of normal incidence, while a greater area of the surface is damaged.

Figure 4.8. The atomic positions for a 1 keV \( C_60 \) molecule incident at \( \theta=60^\circ, \phi=0^\circ \) on Si\{111\} during a 1.75 ps simulation.

Figures 4.10(a), 4.10(b) and 4.11(a) are rayshaded images that show a 250 eV fullerene incident at \( \theta=80^\circ \) and \( \phi=25^\circ \) on the \{111\}, \{110\} and the dimer reconstructed \{100\}(2x1) surfaces. The initial fullerene positions and velocities were identical, with lattice dimensions approximately equal, so the observed differences can be attributed to the differing surface properties. For the \{111\}
surface, the $C_{60}$ molecule is reflected with its centre of mass kinetic energy reduced to 132 eV. The effect of the collision is to impart an energy of 15 eV to the molecule as spin. Vibration of the molecule gives an total internal energy of 34 eV, corresponding to a temperature of 2218 K. Some energy is transferred to the silicon, giving atoms at the impact site a total kinetic energy of 60 eV. The surface initially deforms but rapidly regains its initial shape. A stronger interaction occurs between the fullerene and the $\{110\}$ surface, shown in figure 4.10(b). In this case the molecule sticks and rolls over the surface, pulling silicon atoms from the surface. A similar effect (figure 4.11(a)) results from the collision of $C_{60}$ with the dimer-reconstructed $Si\{100\}(2\times1)$ surface. The interaction is even stronger here due to the corrugation of the surface and little rolling occurs before the molecule finds its binding site.

Figure 4.9. The atomic positions for a 5 keV $C_{60}$ molecule incident at $\theta=60^\circ$, $\phi=0^\circ$ on $Si\{111\}$ during a 1.75 ps simulation.
Figure 4.10. The atomic positions for a 250 eV $C_{60}$ molecule incident at $\theta=80^\circ$, $\phi=25^\circ$ on (a) Si(111), and (b) Si(110). Times are (i) 250 fs, (ii) 750 fs, and (iii) 1250 fs.
Figure 4.11. The atomic positions for a $C_{60}$ molecule incident on Si(100)(2×1). (a) 250 eV at $\theta=80^\circ$, $\phi=25^\circ$, and (b) 1 keV at $\theta=60^\circ$, $\phi=25^\circ$.

Times are (i) 250 fs, (ii) 750 fs, and (iii) 1250 fs.
The final set of images illustrates the types of molecules formed during an energetic interaction where sputtering occurs. Figure 4.11(b) shows $C_{60}$ incident on the reconstructed Si(100) (2×1) surface with a kinetic energy of 1 keV at $\theta=60^\circ$ and $\phi=25^\circ$. The interaction at this energy has features common to all crystal surfaces. The molecule disintegrates on impact with approximately half the carbon atoms reflected from the surface and several silicon atoms ejected. The atoms leaving the surface do so as isolated atoms, dimers, chains, rings and clusters. The majority of atoms within these fragments are carbon, with only one or two silicon atoms usually incorporated. Many of the ejected fragments are in a highly exited state and dissociate rapidly, but the final distribution of clusters cannot be accurately predicted as the energetics of small clusters are not sufficiently well described by the potential [99].

Sputtering occurs in significant quantities if the impacting energy is greater than 2 keV. The calculated yields are an order of magnitude greater than would be expected for single particle impact at the same energy. The results of an investigation into the relationship between angle of incidence and sputtering yield for an incident energy of 5 keV are displayed in Figure 4.12. For each value of $\theta$, the average yield was calculated from 20 simulations. The impact point and $\phi$ were varied over the representative area and directions, so yields are averaged over $\phi$.

The sputtering yield increases as the angle of incidence increases, being a maximum for incidence at around $\theta=40^\circ$. This is a much steeper angle than for single particle impact where the peak is normally around 60°. As $\theta$ moves towards grazing incidence, the majority of the carbon atoms are reflected whilst the damage to the lattice is reduced. The difference in sputtering yield between single atom and cluster impact may be explained by considering the initial events during impact. Single atom impact often leads to channelling of the ion and damage deep within the crystal, while little damage occurs at the surface. The cluster impact guarantees that the surface layers are immediately disturbed, so that as the molecule breaks up, the surrounding silicon becomes irregular. This prevents channelling from occurring and concentrates damage in the first few layers (typically the first 20 Å at the energies studied here) of the surface. As the kinetic energy of the cluster remains with atoms near the surface, ejection can readily occur.
Figure 4.12. The calculated ejection yield as a function of incidence angle for 5 keV impact on Si(111). The curves are smooth fits to the data to guide the eye.
4.3 Investigation of Hydrogen Terminated Si\{100\} Surfaces

The investigation of \(C_60\) interaction with pure and hydrogen terminated \(Si\) surfaces was based on the \(Si\{100\}\) surface as this enabled the effects of various concentrations of hydrogen to be examined. The unterminated 2×1 surface, the 1 hydrogen monolayer (1MLH) covered 2×1 surface and the 2 hydrogen monolayer (2MLH) covered 1×1 surface were examined; these surfaces are illustrated in figure 4.13. The interaction between the \(C\), \(Si\) and \(H\) atoms is modelled by the empirical many-body potential function described in section 3.4.6. As mentioned in sections 3.4.2, 3.4.5, and 3.4.6, the potential gives a reasonable description of all the surfaces studied and has been fitted to model the interactions of fullerenes. A 1.33 monolayer, 3×1 reconstructed surface is also possible [128], but this was not studied. The 3×1 surface consists of alternate monohydride and dihydride units, so its properties can be expected to be intermediate to those of the 1MLH and 2MLH surfaces.

Figure 4.13. The three surfaces studied, viewed at normal incidence. Atoms are represented by circles whose radii decrease with increasing depth, the darker atoms are hydrogen. The arrow indicates the direction of motion of the fullerene in the plane of the surface.

Data was not generated from a statistically representative set of trajectories, instead only a sample set of simulations were run, involving relatively large silicon lattices. Each target was dimensioned with a surface 65 Å × 65 Å and was 20 Å deep, giving 16 layers with 288 \(Si\) atoms per layer, plus 288 \(H\) atoms per surface monolayer. Periodic boundary conditions were applied to the sides of the crystal and the bottom two layers were fixed during the simulation. The system was kept at 300 K by coupling all of the target except the two surface layers to a Berendsen bath [74] with a time-constant of 0.5 ps. Simulations were run for 2 ps, with initial velocities of fullerenes corresponding to energies between
100 eV and 250 eV at various angles of incidence. In each set of three simulations described below, the initial velocity and the impact position of the C60 was the same, so differing results can be attributed to properties of the three surfaces. For clarity in the figures, only a section of the lattice 12 Å thick, centred around the impact point, and with a depth of 14 Å, is drawn. The full width of the computational cell is shown, so in the cases where the fullerene crosses a boundary, the periodicity of the system can be seen. The initial direction of motion of the fullerene is left to right across the page in all cases. Colour images are used to show the energy changes during the higher energy simulations, with the atoms coloured according to their total energy on a log scale as shown in table 4.1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Minimum Energy and Colour</th>
<th>Maximum Energy and Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-7.0 eV Blue</td>
<td>-3.0 eV Red</td>
</tr>
<tr>
<td>Si</td>
<td>-4.6 eV Green</td>
<td>2.3 eV Red</td>
</tr>
<tr>
<td>H</td>
<td>-1.7 eV Cyan</td>
<td>-0.6 eV Yellow</td>
</tr>
</tbody>
</table>

Table 4.1. Colour scales used to show the energy of atoms.

Simulations of 100 eV normal incidence on the three surfaces are illustrated in figures 4.14 to 4.16, and show that hydrogen termination does not prevent reaction. Collision with the bare surface leads to four bonds being formed between the fullerene and the substrate. There is no damage to the C60 cage, but several surface Si atoms are displaced from their original binding sites. Four Si atoms that were components of dimers at the impact point are pushed into the lattice, with a maximum vertical movement of 2.5 Å. The impact on the 1MLH surface is similar to that on the bare surface, but the H coating reduces reaction. Four H atoms that are in direct collision with the C60 are displaced from their surface positions. These atoms travel distances of up to 4.2 Å into the substrate and become interstitials at positions as deep as the fourth Si layer. Four Si atoms in the first and second layers are also displaced from their lattice sites and move distances of around 2 Å deeper into the target. The C60 reacts with two of the exposed Si atoms and bonds to the surface. Impact on the 2MLH surface proceeds in the same way to that on the 1MLH surface, but there is less reaction. Four H atoms are displaced and move up to 2.6 Å into the substrate. One Si atom is also knocked from its original position and moves 1.5 Å deeper into the lattice. After 2 ps, there is one bond between the fullerene and the surface.
Figure 4.14. Atomic positions for a 100 eV C$_{60}$ molecule normally incident on bare Si(100) during a 2.0 ps simulation.

Figure 4.15. Atomic positions for a 100 eV C$_{60}$ molecule normally incident on 1MLH Si(100) during a 2.0 ps simulation.
A second set of simulations was conducted with the same energy and impact point as the first, but with the $C_60$ incident at $30^\circ$ to normal as shown in.
figures 4.17 to 4.19. Impact on the bare surface results in the molecule sticking at the impact point, with only one Si atom displaced from its initial position. Only one bond is formed between the molecule and the Si surface. In contrast to the interaction at normal incidence, the C60 undergoes no reaction with the 1MLH surface. The molecule is reflected from the surface at 20° to normal, but with a kinetic energy of only 9.6 eV. The C60 gains a temperature of 1395 K as 17.0 eV is converted into vibration within the molecule; 73.4 eV is transferred to the surface. In this simulation, the C60 molecule hits the dimer row at an angle of 45°. The collision with the dimer row causes its direction of motion in the plane of the surface to be altered by 71°. Surface atoms are initially disturbed, but no bonds are broken and the surface has regained its initial structure 1 ps after impact. The 2MLH surface is open to penetration because SiH2 units are easily pushed aside. The molecule becomes half submerged in the surface at 0.5 ps after impact. Repulsion between the atoms in the compressed region causes the molecule to rise from the surface, but it remains bound to one Si atom. One silicon and four hydrogen atoms are pushed distances of around 3.4 Å into the lattice and the surface does not regain its structure in 2 ps.

Figures 4.20 to 4.22 show atomic positions at various times for a 150 eV C60 incident at 55° to normal on the three surfaces. The dangling bonds on the bare surface cause the fullerene to stick at the impact point. The top two layers of the Si surface are damaged, with three atoms displaced from their lattice sites and a maximum movement of around 3 Å. Impact on the 1MLH surface results in the fullerene rolling for a distance of several Ångstroms before coming to rest. Collision with the dimer row causes the molecule to be deflected 45° from its original path and it rolls along the direction of the dimer row. As the molecule rolls it knocks five H atoms into the substrate, with those that move the furthest becoming interstitials between the second and third layers. The molecule incident on the 2MLH surface undergoes far less reaction. It is able to roll for almost 20 Å before it comes to rest. During this rolling, five H atoms are knocked into interstitial positions. Whilst rolling, the fullerene forms a bond with one Si atom, but has enough momentum for a C-C bond to be broken and a carbon atom to be partly pulled from the cage before it comes to rest.
Figure 4.18. Atomic positions for a 100 eV $C_{60}$ molecule incident at 30° to normal on 1MLH Si(100) during a 2 ps simulation.

Figure 4.19. Atomic positions for a 100 eV $C_{60}$ molecule incident at 30° to normal on 2MLH Si(100) during a 2 ps simulation.
Figure 4.20. Atomic positions for a 150 eV $C_{60}$ molecule incident at $55^\circ$ to normal on bare $Si\{100\}$ during a 2.0 ps simulation.

Figure 4.21. Atomic positions for a 150 eV $C_{60}$ molecule incident at $55^\circ$ to normal on 1MLH $Si\{100\}$ during a 2 ps simulation.
Figure 4.22. Atomic positions for a 150 eV \( C_{60} \) molecule incident at 55° to normal on 2MLH Si\{100\} during a 2 ps simulation.

Figure 4.23. Atomic positions for a 250 eV \( C_{60} \) molecule incident at 80° to normal on bare Si\{100\} during a 2 ps simulation.
250 eV impact at 80° to normal on the bare surface results in reflection of the \( C_{60} \) and considerable damage to the surface. As the \( C_{60} \) is reflected, a chain...
of Si atoms is pulled from the surface and one atom is knocked 1.2 Å into the lattice. The chain breaks, leaving three atoms bound to the fullerene. The momentum transfer during the chain breaking imparts spin onto the fullerene and causes it to head back towards the surface. After undergoing half a revolution the C60 collides again, 25 Å from the initial impact point. Here it picks up an additional Si atom before impacting a third time, 1.5 ps after the initial collision. The C60 becomes bound to the surface via the Si atoms picked up in the initial collision. A similar impact on the 1MLH surfaces leads to the fullerene picking up one H and two Si atoms. Two H and one Si atom are displaced distances of around 1.2 Å into the lattice. The collision results in one bond being broken in the C60 and causes it to spin. The damaged molecule remains bound to the three additional atoms and travels away from the surface. Impact on the 2MLH surface results in no reaction and no damage to either the fullerene or the surface. The molecule is reflected at an angle of 79° to the surface normal with a kinetic energy of 173.3 eV; 61.4 eV of its initial energy is lost to the surface and 15.3 eV is converted to vibration of the molecule giving it a temperature of 1287 K.

4.4 Conclusions

It has been shown that at relatively low energies (less than 250 eV), C60 remains intact during impact with a silicon surface, the interaction is affected by the orientation of the lattice and the amount of hydrogen on the surface. The bare {110} structure is more susceptible to penetration by the fullerene molecule than the {111} surface. The energy threshold at which a fullerene is reflected from the {100} surface is dependent upon both the surface coating and the angle of incidence. Reflection can occur at higher incident energies if the angle of incidence is away from normal. When reflection does occur, a large proportion of the kinetic energy of the fullerene is transferred into thermal energy. The dangling bonds on the bare surfaces make them reactive and the fullerene is rarely reflected. Hydrogen termination of the surface does not greatly reduce its reactivity with the fullerene. The large momentum of the C60 means that the light H atoms are easily knocked from their surface positions, allowing reaction with the exposed Si atoms. The 1MLH surface is less prone to reaction with the molecule than the 2MLH surface if incidence is at angles close to normal. This is because the SiH2 units on the 2MLH surface are easily displaced, allowing the fullerene to penetrate the surface. When incidence is close to grazing, the 2MLH surface presents a smoother appearance than the ridged 1MLH surface. This results in more reaction with the monohydride surface than the dihydride surface.
Collision at an angle to the dimer row causes a large deflection in the path of the molecule.

When the initial motion of the \( C_{60} \) molecule has a component parallel to the surface, the molecule may roll across the surface after impact. This can lead to atoms being pulled from the surface and sticking to the fullerene. Bond breaking within the fullerene cage is occasionally observed, however no simulation has resulted in \( C \) atoms being removed from the cage. Under certain conditions the fullerene is able to reflect from the surface and pull several atoms with it.

Our simulation results do not show the same scattering behaviour as found by experiment. Most experimental work has been conducted with the \( Si \) surface covered by an oxide passivation layer, this layer will stabilise the surface and reduce its reactivity. In comparison to the graphite surface, the silicon surfaces are far more prone to reaction with the \( C_{60} \) molecule. The propagation of energy into the lattice at low energies is clearly different between the \( Si \) and graphite surfaces. Energy can be transported along individual planes in graphite. In the silicon lattice the greater rigidity of the structure prevents the wave-type motion that occurs in the graphite surface.

At normal incidence with energies above 250 eV, \( C_{60} \) implants into the surface layers of the silicon lattice, breaking bonds and forming a dense region of mixed silicon and carbon. Incidence at 1 keV leads to the production of a disordered region of mixed silicon and carbon, with no sputtering. This process may be useful in the production of thin \( SiC/Si \) interfaces, which are required by the microelectronics industry. As \( \theta \) increases, a proportion of the carbon atoms remain above the lattice surface, either free or loosely bound to the silicon. High incident energies (above 4 keV) cause massive localised damage to the lattice and a large amount of sputtering.
Chapter 5

Fullerene Film Growth on Silicon

5.1 Introduction

Recently there has been great interest in the formation of monolayer and multilayer fullerene films on various surfaces [43-52,151,152]. The electronic and structural properties of well ordered films of fullerenes is a subject of both scientific and potential technological importance. Film growth on silicon is of interest because of the many potential applications of a fullerite-Si interface.

Figure 5.1. AFM topograph of a thick fullerite film grown on silicon at 423 K.
Deposition experiments with fullerenes have been carried out on many substrates, including the (111)(7×7) and (100)(2×1) silicon surfaces [43-46,50,51]. Figure 5.1 shows an atomic force microscope image of a thick fullerene film grown on Si(100), taken from reference [163]. This film was grown at a rate of approximately 0.01 nm/s, in ultra high vacuum, with the C₆₀ powder evaporated at a temperature of approximately 450 °C, and the substrate at a temperature of 150 °C. Typical grain size is around 300 nm, and there is a step height of between 5 nm and 9 nm at the edges of the grains. The X-ray spectrum of this and similar films is dominated by the Bragg peaks of 111, 220, 311 and 222 which are assigned to a fcc lattice with nearest neighbour distance of 1.003 nm. The fullerite (111) planes are parallel to the substrate, and the films are semiconducting.

Figure 5.2. STM image of the Si(100)(2×1) surface with a C₆₀ coverage of approximately 1 monolayer, showing both the c(3×4) and c(4×4) packings. The dark regions are bare regions of the Si surface.
Figure 5.2 is a scanning tunnelling microscope image of the first monolayer of fullerenes on the \{100\}(2x1) surface, taken from reference [43]. The film was grown at a pressure of $10^{-11}$ Torr, with the $C_60$ powder evaporated at a temperature of approximately 370 °C, and the substrate at room temperature. The molecules reside stably in the trough between dimer rows. Local ordering of square and quasi-hexagonal structures is observed in the first layer. The c(4x3) lattice forms the fcc(111) plane as well as the hcp basal plane, whilst the c(4x4) lattice forms the simple cubic (001) plane. STM images show only hexagonal packing above the third layer.

Here, the growth of fullerene films from low energy $C_60$ deposition on a Si surface is studied using a combination of many-body and long-range potential functions [162,163]. Whilst the potentials that we use cannot describe the electronic properties of fullerene films, we can study the structural characteristics of the films and the mechanisms by which film growth occurs. This enables us to observe how the surface temperature affects film growth and how structural properties of the first layers change during film growth. The simulations correctly reproduce the different stacking patterns of molecules on the silicon surface and show the effect of substrate temperature on the local order in the first layer of the film.

5.2 Simulation of Film Growth on Si\{100\}(2x1)

In order to model the growth process it is necessary to have a good description of all interatomic forces experienced by the atoms. A combination of three types of potential function is used to describe the different types of interaction occurring during deposition. Interactions between atoms in the silicon substrate, interactions between the first $C_60$ monolayer and the substrate, and interactions between $C_60$ molecules must be modelled. To allow thermal vibration, the silicon atoms interact with one another via Tersoff’s potential [97], this also allows the surface to relax if necessary during $C_60$ film growth. As the fullerenes have a sub-eV translational energy during film growth, long-ranged forces have a significant contribution to the dynamics of the system. At temperatures above 300 K, $C_60$ molecules rotate freely and can be approximated as spheres. Girifalco’s potential [153] treats the molecules in this way and is used to model $C_60$-$C_60$ interactions. The interaction between a fullerene and the undercoordinated atoms on the silicon surface involves charge transfer from the substrate to the molecule. A Lennard-Jones function between the $C_60$ and individual surface silicon atoms is used to model this interaction. This potential correctly predicts the favoured binding site of $C_60$ to be at the centre of four
dimer pairs on the \{100\}(2x1) surface, but does not specify the orientation of the fullerene. Details of the three potentials used are given in sections 3.4.6, 3.7.3 and 3.7.4, respectively. Although the Brenner potential is included within the model, the interaction between fullerenes is dominated by Girifalco’s potential. Atoms in different molecules are prevented from getting within the interaction distance of the short-range potential at the \(C_60\) energies used in these simulations.

The simulation is started with a bare \(Si\{100\}(2x1)\) surface consisting of five layers of atoms, which is kept at either 300 K or 600 K by coupling to a thermal bath [74] with a time-constant of 1 ps. Periodic boundary conditions are applied to the sides of the system, with free boundary conditions in the vertical direction and the bottom two layers of the target are kept fixed. Due to the long simulation time necessary for the study of film growth, only a relatively small area of the substrate could be modelled. Two surfaces were used; the first was approximately 54 Å x 54 Å with the dimer rows diagonal to the boundary of the simulation region, and the second was 46 Å x 46 Å with dimer rows parallel to the edges of the simulation region. The smaller surface was chosen so its dimensions exactly fitted the periodicity of both cubic and hexagonal stacking in the first layer of film growth. The larger surface was dimensioned such that neither mode of growth could occur without stacking faults. Fullerenes were introduced into the simulation above the potential range of any other atoms or molecules, with an internal energy corresponding to a sublimation temperature of 600 K. A further 0.1 eV kinetic energy was added to the centre of mass of each fullerene, with the velocity towards the surface in a random direction. Experimentally, fullerenes are deposited at a rate of approximately one monolayer per minute. This gives far too long a timescale to be simulated by MD. To reduce the simulation time, a new fullerene is introduced 2 ps after the last \(C_60\) has undergone a collision that temporarily reverses its vertical motion. At the same time as a new fullerene is released, the previous molecule is coupled to the thermal bath, any reflected fullerenes are removed from the system when they move out of the interaction range of all other atoms. The following figures show the film, viewed at normal to the surface. For clarity only the dimer pairs of the \(Si\) surface are drawn and atoms are coloured according to their depth.

Figure 5.3 contains snapshots from a simulation in which 25 fullerenes were deposited upon the 54 Å x 54 Å silicon surface, with the silicon atoms kept at an average temperature of 300 K. The fullerenes are mobile in the first layer and collisions with incident molecules cause rearrangement of the fullerene film. The fullerenes preferentially lie in the trough between dimer rows and the majority of motion occurs along the direction of the dimer row. As more molecules accumulate on the surface, they congregate into groups and the film is

147
stabilised. At this temperature, the molecules are rarely dislodged once they have settled into the minimum energy position at the centre of four dimer pairs. This results predominantly in a cubic packing in the first layer, but as the dimension of the surface is 54 Å and the lattice constant of the fullerite structure is around 10.4 Å, a stacking fault is introduced and some hexagonal packing is observed. A mixture of cubic and hexagonal stacking is in agreement with the reported STM results. Molecules that impact above a closely packed region in the first monolayer can settle into the hollows between molecules. The fullerenes are stable in these positions as they have at least four near neighbours and are still in the range of the surface-C60 interactions. In the time simulated here, there is no migration of molecules from these sites to the Si surface. Hence the second layer begins to form prior to the completion of the first monolayer.

Figure 5.3. Positions of C60 molecules at various stages during film growth on a 54 Å x 54 Å region of Si(100)(2×1) at 300 K.
To investigate the effect of substrate temperature, the simulation was repeated with the temperature increased to 600 K. The results of this simulation are shown in figure 5.4. The growth process is similar, but the higher temperature increases the mobility of the fullerenes. During interaction with other molecules, fullerenes are able to escape from the minimum energy position for an isolated molecule and move into a position that allows the $C_{60}-C_{60}$ separation to be much closer to the ideal fullerite structure. This results in a hexagonal packing, where fullerenes lie alternately between the centres of four or two dimer pairs along the troughs between dimer rows. The nearest neighbour distances for cubic packing are 10.86 Å, while hexagonal packing results in an average of 10.24 Å (two neighbours at 9.6 Å and four at 11.52 Å), compared to a distance of 10.02 Å in perfect fullerite. The change in distances between molecules causes an increase in the stacking fault relative to the 300 K simulation.
As the dimensions of the simulated region can cause stacking faults and so have an effect which type of stacking is preferred, a third simulation was run where neither type of stacking would cause any faulting. The dimer rows are parallel with the periodic boundaries and the silicon is dimensioned 46 Å × 46 Å. The results of a 300 K simulation with this lattice are shown in figure 5.5. The stacking is almost perfectly hexagonal, with one void in the surface layer. The small size of the system and the rapid deposition of fullerenes is probably responsible for this faulting. The simulation was run until several layers had formed. The layers formed a faulted hcp structure with the stacking sequence ababeb; although fullerite sometimes occurs in this form [164], it is usually observed in the fcc structure [165]. The truncated $C_{60}-C_{60}$ pair potential function used is not sufficiently accurate to correctly differentiate between the two closed packed forms.

Figure 5.5. Positions of $C_{60}$ molecules at various stages during film growth on a 46Å × 46Å region of Si(100)(2×1) at 300 K.
5.3 Conclusions

We have been able to simulate the growth of multilayer $C_{60}$ films on $Si(100)(2\times1)$. Hexagonal stacking predominates in the first layer, but some cubic stacking can occur. The preference for cubic stacking is increased at lower substrate temperatures. The fullerenes are fairly mobile on the surface and congregate into regularly packed groups with stacking faults between the groups. Impact of molecules onto a one monolayer covered region initiates growth of new layers before the first layer is completed.
Chapter 6

Ion Bombardment of Graphite

6.1 Introduction

The recent advent of microscopies such as scanning tunnelling microscopy (STM) and atomic-force microscopy (AFM), that are capable of atomic resolution, has enabled the consequences of individual ion impacts on solid surfaces to be studied. Similar features are produced on the surfaces of most materials by low dose keV ion impacts, and consist of a crater surrounded by an annular ridge of adatoms [53]. In contrast to this behaviour, bumps not craters are formed on the surface of ion bombarded graphite [53,166-168]. Figure 6.1 shows a $60 \times 60 \text{ nm}^2$ STM image, taken from reference [167], obtained on highly ordered pyrolytic graphite (HOPG) bombarded with 500 eV $Ar^+$ at normal incidence. The figure shows protrusions of irregular shape on the originally flat surfaces.

Several different mechanisms for the formation of these bumps have been proposed by various groups of authors, and are discussed by Li et al. [167]. The models are either based on defect induced elastic strain deformation, or an attempt to correlate the measured features with the energy deposited in damage at or near the surface. A thermal spike contribution to bump formation has also been suggested and another model considers the accumulation of interstitials along the ion track. However none of the models put forward can account for all the experimental observations. There is also some contradiction in the reported experimental findings; for instance a link between the bump volume and the energy deposited at the surface has been reported for ion energies above 10 keV [166], whilst no energy dependence is reported for lower ion energies [169,170]. These proposed models are qualitative and non-atomistic in nature and some do not account for the time evolution of the process.

The limitations of the models can be avoided by employing MD simulation to study the dynamical processes by which the bumps are formed [171]. The results of a simulation using Tersoff's potential are presented in section 6.2. As bump formation must involve a change in the interlayer spacing in graphite and Tersoff's potential does not describe the interlayer binding, it was necessary to conduct some simulations to see if the addition of long ranged forces would have an effect on the results of the simulations. Simulations of bump
formation were conducted using the potential due to Heggie [58] and are described in section 6.3.

![STM Image](image)

**Figure 6.1.** An STM image of HOPG after bombardment by 500 eV Ar ions at normal incidence.

The proposed mechanism for bump formation is essentially independent of the species of the bombarding ion, *as the ion simply knocks one or more carbon atoms into interstitial positions between graphite layers*. Hence the dimensions of bumps can be expected to be related in some way to the number of near surface interstitial atoms produced per ion impact. This in turn will be a function of the ion energy and the energy required to create an interstitial in the graphite structure. Section 6.4 describes the calculation of the displacement threshold energy for an atom in the graphite lattice. A lower bound of 34 eV was calculated for this energy.
6.2 Simulations Using Tersoff’s Potential

In order to investigate the process of bump formation, the bombardment of a graphite lattice by a 500 eV carbon atom was studied. Interactions were modelled by Tersoff’s carbon potential, connected to a screened Coulomb potential at short separations. The graphite target was modelled as seven graphite layers, dimensioned approximately 70 Å x 70 Å, giving a total of 14372 atoms. A trajectory was chosen where the ion impinged on a surface carbon atom.

In this trajectory, the collision is such that the surface atom is knocked from its lattice site, whilst the ion is deflected, but passes through several more layers. The purely collisional phase of the cascade is over in 0.1 ps. The primary knock-on atom (PKA) acquires about 120 eV and recoils a distance of about 10.5 Å, leaving a vacancy in the surface graphite layer. Atomic positions during the simulation are shown in figure 6.2; as the processes of main interest occur between the first and second layers of the graphite target two sets of figures are given. The first set shows the graphite surface, whilst all the surface atoms except for the PKA have been removed in the second. The PKA collides with the second graphite layer, but does not pass through it, hence it becomes trapped between the two surface graphite layers. The PKA is reflected back and forth between the two layers, and loses its kinetic energy to them.

During the evolution of the cascade, some atoms in the surface layer of the crystal are displaced in the direction of vacuum. At 0.04 ps, 10 atoms are already displaced by distances larger than 0.3 Å, and at 0.24 ps, about 100 atoms have risen above the original position of the surface layer. A plateau like region develops with a maximum height of around 1.1 Å. The maximum height of the bump changes very little after this time, but the lateral dimensions of the bump continue to increase throughout the simulation. The edge of the bump travels with a velocity of around \(3 \times 10^5\) cm/s (i.e. at the typical velocity of sound in a solid). The atoms in the second layer undergo an inward motion and approach the third layer. The depression of the second layer closely mirrors the evolution of the first layer. At 0.04 ps, 12 atoms have been displaced between 0.4 Å and 1.5 Å towards the third layer, whilst about 100 atoms have moved towards the third layer by a time of 0.24 ps.
Figure 6.2. Atomic positions during bump formation in graphite after normal impact by a 500 eV C atom. The ion is coloured red, and the PKA is green. (a) All atoms shown, (b) Surface layer removed (except for the PKA).
The transversal extent of the bump (several tens of Å) is much greater than its height (around 1 Å). These quantities characterising the bump dimensions are comparable in magnitude with experimental findings [167]. The simulation was continued for several picoseconds, and the bulk of the bump was seen to remain fairly stable. In particular the bump height does not decrease during this time.

The results therefore indicate that bumps are caused by an interstitial atom between surface graphite planes. The proposed mechanism for the formation of bumps during the early stages of ion bombardment of graphite, is in terms of interlayer interstitial recoils. The incoming ion undergoes a collision with an atom in one of the graphite surface layers, knocking it into an interstitial position. The interstitial atom is trapped between two graphite layers and is reflected back and forth between them. As this happens, the kinetic energy of the atom is transferred to the two graphite planes, causing them to move apart.

6.3 Simulations Using Heggie’s Potential

Tersoff’s potential cannot describe forces between separate graphite planes, and this deficiency in the modelling of interactions may affect results of the simulations presented in section 6.2. However, Heggie’s potential was produced to model vacancies and interstitials in diamond and graphite, and includes a description of interlayer forces in graphite. The investigation of the description of C60-graphite interactions by differing potentials in section 3.8.3 showed qualitative agreement between Tersoff-type potentials and the proximity cell potential. A similar investigation was carried out to verify that the inclusion of interlayer terms in the potential function did not prevent the formation of bumps on the graphite surface. A single simulation, where ion bombardment of graphite would produce an interstitial between two graphite layers, was conducted using the proximity cell potential.

To ensure that an interstitial was produced, the impact point on the surface, shown in figure 6.3, was chosen such that the energy transferred to one surface atom was sufficient to knock it into a position between the two layers. Figure 6.4 shows atomic positions during a 300 fs simulation of 500 eV C atom bombardment at normal incidence. As the proximity cell potential is extremely costly to evaluate, the smallest possible system was modelled to enable a sufficiently long simulation time. The graphite surface was represented by two graphite planes, dimensioned 40 Å × 40 Å, giving a total of 1326 atoms. The incoming ion retained enough energy to pass through the second layer and travel out of the simulation region.
Figure 6.3. Impact position of the 500 eV carbon atom. The PKA is shaded grey.

The simulation was run for as long as possible, but was stopped when the effects of reconstruction at the edges of the layers became too great. The ion collides with the PKA, knocking it into an interstitial position between the layers. The ion retains much of its energy and passes through the second graphite layer without causing any further damage. The PKA is displaced laterally by around 10 Å as it moves to an interstitial position, it quickly loses its kinetic energy by collision with the two graphite planes and remains between the two layers for the rest of the simulation. As the kinetic energy is transferred from the PKA to the graphite planes, atoms in the vicinity of the PKA gain momentum and the interlayer spacing increases. The bump reaches a maximum height of around 1 Å after 0.2 ps and is stabilised by the presence of the interstitial atom.
Figure 6.4. Atomic positions during bump formation in graphite after normal impact by a 500 eV C atom. The interstitial atom is shown in (f) by viewing between the graphite planes with edge atoms removed.
As the height of the bump is around 1 Å, this indicates that it is stabilised by repulsion from the interstitial rather than bonding between the interstitial and the two graphite planes. The largest displacement due to a bonded interstitial would occur when the interstitial bonded between two atoms in adjacent planes, that were stacked one above the other in the c direction. This case has been calculated by Heggie using his proximity cell potential [58]. He obtained an interstitial formation energy of around 7 eV, in good agreement with experiment. The interstitial lies directly between the two atoms and forms one bond with each. The two in-plane atoms become almost sp$^3$ hybridised ($\langle |p_z| \rangle = 0.33$), with bond angles near those of the tetrahedral structure. The bonds formed by the interstitial are 1.62 Å long, due to the incomplete hybridisation of the in-plane atoms. The nearly sp$^3$ hybridised atoms are each displaced by around 0.5 Å due to their tetrahedral configuration. This results in an interlayer separation of around 4.2 Å for atoms in the vicinity of the interstitial; an increase of only 0.89 Å. As an almost equal depression and bump are formed, the bump height would only be around 0.45 Å. Hence, we can conclude that the bump observed in the simulation is not caused by a bonded interstitial bridging the gap between two layers. The results of calculations using Tersoff’s potential also predicted a bump height of around 1 Å. As interactions are cut off at 2.1 Å with this potential, there is no interaction between the interstitial and the graphite planes once the bump is formed.

6.4 The Displacement Threshold Energy for Graphite

The initial event in radiation damage of a crystal is the sudden transfer of a large kinetic energy to atoms within the lattice. This localised input of energy leads to the formation of vacancies and interstitial atoms, and a damaged region is produced in the crystal. Molecular dynamics simulations were conducted to obtain an estimate of the energy required to produce permanent damage in the graphite lattice, as a function of the initial direction of motion of a displaced atom. The initial event in the radiation damage was modelled as an instantaneous gain of momentum by one atom in the crystal. This is not a particularly accurate approximation for radiation damage due to ion bombardment, as the incoming ion would be expected to experience several collisions in any small region and eventually undergo reaction and bonding at the end of the ion path. Unfortunately, making the simulation large enough to incorporate a surface and contain the whole ion path is infeasible, due to the computation resources required to calculate a representative set of trajectories. The model used is a much closer
approximation to the case of radiation damage by light particles such as electrons or neutrons, where the projectile would be expected to travel a considerable distance between collisions. The results can also give qualitative information about the initial transfer of energy from the primary knock-on atom (PKA) to the rest of the lattice in the case of heavy ion bombardment [72,172].

The second parameterisation of Brenner's potential was used to describe interactions as this gives a good description of the graphite structure whilst predicting stretching force constants of bonds to a reasonable accuracy. The potential is also fitted to the vacancy formation energy in graphite. No interlayer terms are included in the potential, but this can be expected to have a negligible effect on the calculated displacement threshold energy. It should be noted that the final defect structures obtained from the simulations may be affected by the lack of the weak interlayer forces. The system consisted of a cuboid 26.1 Å × 25.2 Å and 26.8 Å deep, containing 1920 atoms in 8 planes of 240 atoms. Periodic boundary conditions were applied in all three cartesian directions. By simulating a relatively large volume compared to references [72,172] (576 and 94 atoms respectively), boundary effects of the region are negligible and the need to introduce damping is avoided. As there are no interlayer forces, atoms at the sides of the computational box were fixed to prevent the graphite layers from drifting. The lattice was initially at 0 K, as adding heat to the simulation would mean that there was no unique starting point to any trajectory and hence require a representative set of trajectories to be simulated for each direction and energy investigated. The effect of temperature on the displacement threshold energy has previously been investigated for diamond [172] and has been found to be negligible, at least up to temperatures of 300 K.

An atom at the centre of the computational cell was chosen to be the PKA, and given an initial kinetic energy in a chosen direction. Due to the symmetry of the graphite structure, the representative directions are described by $\frac{1}{2}$ of a sphere (an angle between 0° and 90° to the graphite plane, and an azimuthal angle between 0° and 60°). The angles are defined in figure 6.5; $\theta = 0$ corresponds to motion totally within the graphite plane, and $\phi = 0$ corresponds to motion along the direction of a bond. There are two distinct atomic configurations in the graphite structure, as an atom may either lie directly between two atoms in adjacent planes, or between the centres of two hexagons. An investigation was conducted for each of these two cases, denoted as AA and AB configurations, respectively. The initial direction of motion of the atoms was sampled in 10° steps, giving 64 directions to calculate for each of the two cases.
For a given direction, an energy below any possible displacement threshold was first added to the PKA and the simulation run. Simulations were then run with 1 eV increases in the energy of the PKA until a permanent defect was detected. A permanent displacement was defined as a change in bonding within the lattice that persisted for 500 fs. As the graphite planes can distort a large amount without any bonds being broken, defects were checked for by examining the neighbour lists of atoms. A change in the coordination of any atom was assumed to signify the possible production of a defect. The final states of trajectories that resulted in a displacement were checked by computer visualisation to ensure that the defect couldn’t disappear due to reconstruction. Further simulations were then run at slightly higher energies for directions where the initial results were inconclusive. The first energy at which a permanent defect occurred was taken as the displacement threshold energy for that particular direction.

The results of the calculations are shown in figures 6.6 and 6.7, plots are given against both $\phi$ and $\theta$ or both types of atom. Averaging the results over the $\sqrt{2}$ sphere gives a value of 34.0 eV for an AA stacked atom and 34.5 eV for an AB stacked atom. Due to the anisotropy of the graphite structure, values vary from 22 eV to 105 eV depending upon the initial direction of motion of the atom. The minimum energy arises when the atom can travel the furthest before collision with another atom. This is especially evident for the in-plane displacements ($\theta = 0$ in figures 6.6(b) and 6.7(b)) where the minimum occurs at $\phi = 45^\circ$. When $\theta$ lies between 30° and 80° the calculated displacement threshold is almost constant with a value around 30 eV.
Figure 6.6. Displacement threshold energy for an AA atom. (a) Against initial angle to the plane, for various azimuthal angles. (b) Against initial azimuthal angle, for various angles to the plane.
Figure 6.7. Displacement threshold energy for an AB atom. (a) Against initial angle to the plane, for various azimuthal angles. (b) Against initial azimuthal angle, for various angles to the plane.
Some structures resulting from radiation damage are shown in figure 6.8. In the cases of in-plane damage, a faulted graphite plane containing 4, 5, 6, 7 and 8 membered rings is produced. When the initial direction of the atom has a component perpendicular to the plane, a vacancy is formed near the initial position of the PKA and an interstitial atom is produced. The interstitial may be unbound but trapped between two graphite planes, or may be bound to one or both the planes.

Figure 6.8. Examples of the structures resulting from simulations to determine the displacement threshold energy. The initial velocity of the PKA was in-plane for (a) and (b) and at 40° and 50° to the plane for (c) and (d).

These calculations give a lower bound on the impact energy required for a single ion to displace atoms within a graphite target. Although the resulting structures are stable for the time of the simulations, some may be relatively short
lived due to the close separation of the defects produced. Similar studies with silicon [72] have indicated that modifying the definition of a stable defect to include a minimum displacement distance of $\frac{1}{2}$ lattice unit (4.1 Å in silicon) gives a result in much better agreement with experiment. For instance, the calculated displacement threshold energy increased from approximately $\frac{1}{2}$ to $\frac{3}{2}$ of the experimental value, and the correct anisotropy was only given using the modified definition. However those results are based on the generation of frenkel-pairs, so cannot be directly compared with calculations for graphite where the defects have a very different structure. The average value of 34 eV calculated for graphite can be compared to the displacement threshold energy of 50 eV calculated for diamond using a similar method [172]. This suggests that the different structure of the two allotropes causes a significant difference in their radiation damage thresholds. The cohesive energy of graphite is 7.374 eV per atom, hence an energy of 14.748 eV is required to break the three covalent bonds on one atom. Although there are significant energy barriers to be crossed for in-plane reconstruction to occur, most cases of damage result in the PKA moving to a position between two graphite layers, followed by reconstruction around the defect site in the plane. The energy required for the interstitial to overcome any barrier to migration cannot account for the additional energy required (an average of around 20 eV) for defect production. The additional energy required is due to the rapid dissipation of kinetic energy into vibration of the graphite lattice during the initial stages of defect production.

6.5 Conclusions

There is considerable agreement between the results of MD simulation and experiment. The proposed mechanism for bump formation in graphite during ion bombardment is the production of weakly bound interstitial atoms between the surface graphite layers. The mechanism is essentially independent of the bombarding ion used. An energy in excess of around 34 eV must be transferred to the PKA in order to knock it out of a graphite plane and into an interstitial position. Since completing this work, we been made aware of a recent experimental determination of the displacement threshold energy by Steffen et al. using low energy ion irradiation [173,174]. Their experiments resulted in an estimate of 35.8 ± 1.0 eV for the displacement threshold energy, in very good agreement with our calculations.
Chapter 7

Ion Bombardment Of Polyethylene

7.1 Introduction

Bombardment of polymers by energetic ions has a number of applications, e.g. the production of semiconductors by ion-beam lithography [175,176]. A pattern is first created in a polymer resist (e.g. polymethylmethacrylate) with an electron or ion beam, then the resist is used as a mask during reactive ion etching of the semiconductor. Another application is in surface analysis. Secondary Ion Mass Spectrometry (SIMS) is a valuable technique for the chemical analysis of polymers [177-180], where the nature of fragments ejected during ion bombardment is analysed to study the composition of the target. The bombardment of polymers by energetic ions produces dramatic structural changes due to disruption of the original chemical bonding. This disruption occurs as chain scission, cross linking and carbonisation and causes gas evolution and ejection of polymer fragments with a wide distribution of molecular weights.

While many groups have studied the energetics and dynamics of polymer chains via constrained MD (see for example references [146-148]), relatively little work has been done to investigate radiation damage to polymers. Taylor et al. [21,122,177,178] have studied 500 eV Ar bombardment of \( \text{C}_2\text{H}_3 \), \( \text{C}_3\text{H}_5 \) and \( \text{C}_5\text{H}_9 \) films absorbed on Pt\( \{111\} \). The majority of ejected clusters were the result of the dissociation of a single adsorbate. Other clusters were produced by the reaction of two adsorbates or the reactions of ejected clusters with other clusters or adsorbates.

As a preliminary investigation of the ion bombardment of polymers, the effects of 1 keV \( \text{Ar} \) bombardment of the surface of a single polyethylene crystal were studied by MD. Polyethylene was chosen as the model system for this study as it is the simplest polymer. The radiation damage caused chain scission, cross linking and carbonisation of the target. The evolution of gas and loss of volatile species in the form of ejected clusters was analysed and the numbers and types of ejected molecules were quantified. The results indicate that a single impact trajectory may be divided into two parts, the first having a duration of under 0.4 picoseconds and the second lasting for many picoseconds. The initial impact causes bond breaking and sputtering of atoms and small hydrocarbon radicals. At
later times recombination takes place between fragments remaining within the target, producing molecules of varying size that diffuse through the target and escape.

7.2 Details of the Calculation

The Brenner hydrocarbon potential is used to model the interaction between $C$ and $H$ atoms in polyethylene. This many-body potential has been fit to the properties of bulk diamond and graphite as well as many hydrocarbon molecules and radicals; it should therefore be accurate at describing the bonding within polymer chains and the reactions between radical molecules. Because the potential is short ranged, it is sufficiently quick to evaluate to allow large simulations to be performed. It has the disadvantage that long range interactions are ignored, so there is no intramolecular binding described in the model. Potentials to describe nonbonded interactions are incorporated into MD studies of polymers [146-148,150] and have been used with the Brenner potential [126,149]. These methods require atoms that are to experience long range interactions to be specified at the beginning of the simulation and preclude the possibility of reaction and bonding between molecules. This study was specifically concerned with large disturbances of polymer chains, where bond breaking and bond formation were expected, so the methods mentioned above were not suitable. By including an additional cutoff function as described in section 3.7.1, we have developed long-ranged potentials that do not preclude the possibility of reaction. Unfortunately, the number of atoms that need to be considered reduces the speed of computation to a level where simulation of many trajectories is infeasible for large systems. Therefore, non-bonded interactions are ignored in these simulations, so separate polymer chains do not interact in the undisturbed crystal. This should have little effect on the initial part of trajectories, as atoms start on lattice sites and only high energy collisions occur. Care needs to be taken when analysing the behaviour of the system at later times in the trajectories, where low energy motion in the target and diffusion of chain fragments would be affected by long range interactions.

The second parameterisation of the Brenner potential [65] was chosen for this study because it gives a far better reproduction of $C$-$C$ bond stretching force constants than the first. Bond lengths are not predicted quite so well with this parameterisation, but for this simulation the force constants were regarded as being more important. For the minimum energy structure of a polyethylene chain the potential gives energies of 3.54 eV and 4.36 eV and lengths of 1.553 Å and 1.072 Å in comparison to experimentally determined values of 1.541 Å and...
1.073 Å for C-C and C-H bonds respectively. Ar-Ar, Ar-C and Ar-H interactions are described by a smoothly truncated ZBL 'universal' potential. The ZBL potential is truncated between distances corresponding to 90% and 110% of the sum of the average bond radii of the atoms involved, as detailed in section 3.6. This restricts the Ar interactions to a similar distance to the C-H interactions whilst ensuring that forces are a continuous function of atomic separation and decay smoothly to zero at the cutoff. A fixed timestep length of 0.15 fs was used in all simulations, resulting in a maximum change of 0.036% in the total energy of the system during any single trajectory.

Figure 7.1. Atomic positions showing one surface fold and a section of the crystal surface.

In all simulations, the target was a cuboid of orthorhombic polyethylene crystal with a unit cell 7.418 Å × 4.946 Å × 2.546 Å; the c-axis of the unit cell was vertical and the a and b axes parallel to the sides of the simulation box. The polyethylene chains were truncated at the base of the target, whilst the top surface was capped by chain folds, each consisting of five CH₂ segments. The chain folds were created by adding C and H atoms in approximate positions to a truncated crystal and annealing the structure of the surface whilst keeping the bulk lattice atoms fixed. The optimisation of the structure was repeated for twenty random starting configurations of the surface folds, and the lowest energy structure was selected. This configuration is in excellent agreement with predictions for the surface folds on flat lamellar polyethylene crystals [181,182] and is shown in figure 7.1. The calculated energy of the atoms involved in folds differs by less than 0.02 eV from atoms in the bulk material. The target surface is depicted in figure 7.2. Periodic boundary conditions were applied to the sides of the crystal to prevent escape of hydrocarbon fragments and to stop polymer chains from falling.
away from the crystal; free boundary conditions were applied to the top and bottom surfaces. The distribution of molecule types throughout the system at various times was analysed using the recursive algorithm described in section 2.7.

Figure 7.2 Target surface with and without surface folds, viewed at normal incidence and showing unit cells. The incident direction of the argon atom is shown along with the unit cell axes, the c-axis is out of the page.

Three sets of simulations were completed, all with 1 keV argon atoms incident at 60° to the surface normal and parallel to the a-axis of the unit cell. The initial velocity of the incident atom was restricted by the available computational resources. A greater kinetic energy would require a larger target size and an increase in the length of the simulation, leading to prohibitively large CPU requirements. The incident direction of the argon atom was chosen to be 60° to normal in order to prevent the atom from passing through the lattice by channelling along the c-axis. Thirty single impact simulations of 2 ps duration were carried out, with the argon atoms incident over a representative area that was the surface of one unit cell. To get an efficient coverage of the target area, the impact points were selected from a two-dimensional Halton sequence [75]. A smaller set of five trajectories, similar to the first set but for a time 4 ps was simulated to examine the behaviour of the system at longer times. A multiple impact simulation of 5 consecutive 4 ps trajectories, with impact positions over the whole surface was carried out to study the effect of collisions occurring near previously damaged sites. For the single impact simulations, a target with a surface 52 Å × 49 Å, and 42 Å deep was used. This gave a lattice consisting of 7 × 10 × 15 unit cells with a top surface of folded chains, creating a total of 13650 atoms (70 folded chains of C65H130). The target is sufficiently large so that the argon atom does not re-enter a previously damaged region and deep enough so that very few atoms escape through the base of the simulation box. For the
multiple impact simulation, a slightly smaller (37 Å × 40 Å × 42 Å) lattice was used. This contained 5 × 8 × 15 unit cells plus the surface folds (7800 atoms in 40 folded chains of C65H130). To prevent a build up of energy in this simulation, the lattice was connected to a zero K Berendsen thermal bath [74] with a time constant of 100 fs for the last 1 ps of each trajectory.

7.3 Single impact simulations

Figure 7.3 shows the average mass spectrum of ejected molecules at 2 ps after impact, for thirty simulations. The mass spectrum consists of atomic and molecular hydrogen, plus hydrocarbon fragments with masses up to 280 AMU (C20H39). Ejected molecules are mostly hydrogen deficient chain segments of the form CxHy, where 2x-2 ≤ y ≤ 2x. The largest peak is due to atomic hydrogen, although more hydrogen atoms are ejected in H2 molecules. The third highest peak corresponds to C2H4, and far more atoms are ejected as components of C2H3y molecules than CHy molecules. More hydrogen is ejected as part of C2H3y molecules than as either atomic or molecular hydrogen. Breaking of the polymer chains would be expected to produce a large quantity of hydrocarbon radicals, but it appears that many of these react and form stable molecules before leaving the polymer. The frequency of ejected molecules drops sharply for x > 2. The mass of ejected molecules is plotted against time of ejection in figure 7.4.

Figure 7.3. Histogram showing the average mass distribution of ejected molecules per single impact after 2 ps.
Figure 7.4. The mass of ejected molecules against time of ejection for thirty single impact simulations.

Figure 7.5. The average number of molecules sputtered against time, for the three predominant ejected molecules.
Many atoms and small molecules are ejected during the first 0.4 ps of each trajectory and ejection continues at a slower rate for the rest of the simulation. The amount of time before a large molecule can escape increases with its mass. Atomic hydrogen, molecular hydrogen and \( C_2H(2-4) \) molecules leave the target throughout the simulation. Figure 7.5. shows that much of the atomic hydrogen is sputtered during the initial high energy collisions. After the first 0.4 ps, the rate of ejection is almost constant for the three molecules, with \( H_2 \) ejected at the fastest rate and \( C_2H_4 \) at the slowest rate. Figure 7.6 illustrates the initial depth of all atoms ejected during 2 ps. The depth profile shows an exponential decay for both elements, but hydrogen atoms can escape from greater depths than carbon.

\[ \text{Figure 7.6. Histograms showing the average depth profile of sputtered atoms per single impact after 2 ps.} \]

The time taken for atoms to leave the target increases with their initial depth. It should be noted that the omission of nonbonded interactions means that the number of large molecules ejected and the number of atoms ejected from deep within the target may be overestimated. Intramolecular binding would be expected to reduce the rate of diffusion of chain fragments. A total of 1286 \( H \) and 483 \( C \) atoms were ejected within 2 ps during thirty single impact simulations. This gives a hydrogen to carbon ratio of 2.66:1 in the ejected atoms and shows that the target can become hydrogen deficient. The number of \( C-C \) and \( C-H \) bonds broken and
cross links formed can be estimated from changes to the coordination of carbon atoms within the target. These changes are shown in figure 7.7.

![Figure 7.7 Average time profile of lattice carbon atoms with changed coordination during single impact trajectories.](image)

The initial impact causes bond breaking and leads to undercoordinated C atoms and free H. The gradual reduction of the number of these is due to the escape of fragments from the target and some rebonding that takes place at a slow rate. A small number of molecules that are not simple chain fragments are formed by the recombination of hydrocarbon radicals and atomic hydrogen. There are between two and three C atoms per impact that obtain 3 bonded C neighbours, when this happens it occurs during the first 0.2 ps after argon impact. The low number of C atoms with three C-C bonds shows that very little cross chain linking occurs. At 2 ps the lattice contains molecules of varying molecular mass, very few molecules are created that are larger than the initial chains (65 CH2 segments). In thirty simulations only 15 molecules with 70 or more C atoms were created, 14 during the first 0.2 ps after argon impact. These large molecules are typically hydrogen deficient by around 4 atoms. Approximately two C atoms with three C-H bonds are created in the first 0.2 ps, but this number gradually rises to over four by 2 ps as free hydrogen recombines with chain fragments within the target.
Figure 7.8. Changes in the amount of hydrogen (as \( H \) and \( H_2 \)) in the system during the 2.0 ps after ion bombardment.

Figure 7.8 shows how the amount of atomic hydrogen within the crystal decreases during the 2.0 ps after impact. The total amount of molecular hydrogen rises, but does not account for all of the removed atomic hydrogen as some combines with hydrocarbon radicals trapped within the polymer. At 2 ps there are many small molecules and hydrogen atoms (approximately 10 \( H_1 \), 10 \( H_2 \) and 7 \( C_2H/(1-4) \) per impact) with typical kinetic energies of around 0.1 eV that diffuse throughout the target.

Although the number of 4 ps simulations completed is too small to yield good statistical data, the results do support the trends identified in the shorter simulations. In particular, the proportion of atomic hydrogen within the target continues to decay as \( H_2 \) and \( C_2H_4 \) molecules are formed. The proportion of \( H_2 \) and \( C_2H_4 \) in the spectrum of ejected molecules increases as these molecules diffuse from the surface. A video of a sample 4 ps trajectory has been produced [80].

In summary each trajectory has two components. During the first 0.2 to 0.4 ps after impact, many free hydrogen atoms and hydrocarbon radicals are created with some being sputtered from the surface. At later times these diffuse through the crystal and recombine to produce more stable molecules, some of
which escape from the target. Large molecules with very little kinetic energy are formed by the breaking of polymer chains and these drift free of the target over a time of many picoseconds. There is little evidence of cross linking that increases the molecular mass of polymer chains.

7.4 Multiple Impact Simulation

Multiple impacts around the same site result in considerably more damage to the target than single impacts. Molecules of greater size (up to $C_{36}H_{69}$) and a total of 771 $H$ and 368 $C$ atoms were ejected during five impacts. This gave a hydrogen to carbon ratio of 2.095:1, the ratio is lower than for single impacts because there is a greater proportion of large chain segments ejected from the target. The increased number of chain segments ejected causes the number of atoms ejected per impact to be around 3.5 times that for single impacts. There is no evidence that multiple impacts increased cross chain linking, instead the damage to the target increases with each impact and the regular structure of the lattice is broken down. This allows molecules with large masses to be ejected more frequently than in single impact simulations. These results should be treated with caution, as the lack of long-ranged interactions will exaggerate both the number of molecules sputtered and the lack of order within the target. The greater amount of damage leads to the production of new molecules by recombination of atoms and radicals. During the five impacts, one $C_2H_6$ and two $CH_4$ molecules were formed, along with several other molecules of the form $C_xH_y$, where $y > 2x$, that could not be simple chain segments.

7.5 Conclusions

It has been shown that a single 1 keV argon atom can cause changes in the structure of a polyethylene crystal over a time of several picoseconds. The spectrum of ejected species is dominated by atomic and molecular hydrogen, but includes large chain fragments containing up to 20 $CH_2$ units. During the first 0.4 ps of each impact, bond breaking creates highly reactive hydrocarbon radicals and free hydrogen atoms. These are sputtered, or recombine to produce more stable molecules that can diffuse through the target and escape from the surface at a later time. The heavier molecules take a longer time to drift free from the target. To examine these processes completely, an investigation far larger than this preliminary study is required. Simulations need to be conducted for a greater time (at least 10 ps) to study the diffusion processes completely and will require a larger target. Simulations of this duration will necessitate the addition of long
range interactions to allow a better description of diffusion within the target and to ensure polymer chains retain physically realistic configurations. At present the energy range of bombarding atoms that can be studied is severely limited by computing resources.
Chapter 8

The Interaction of Hydrogen With C$_{60}$

8.1 Introduction

The stability and size of the C$_{60}$ molecule suggests that it might be possible to produce new materials by implantation of atoms into the C$_{60}$ cage structure. A short time after the discovery of the C$_{60}$ molecule, evidence was obtained that a single lanthanum atom could be trapped inside the cage [54], and the trapping of other species such as potassium has also been reported [55]. The evidence for the existence of the metal atom trapped within the cage was a combination of FT-ICR mass spectra and experiments which showed that externally attached metal atoms behave in a radically different way, i.e. they react easily and are readily knocked-off the molecule. The reported success with metal atoms suggests that it might be possible to implant other species, such as hydrogen, within the C$_{60}$ structure. There are a number of possible applications for H trapped within the C$_{60}$ structure. Endohedral complexes would provide a unique possibility to tailor specific properties of C$_{60}$ systems on a molecular level. Modifications in the electronic and phonon spectrum of these materials are expected. A non-bonded hydrogen atom inside a C$_{60}$ cage would be a paramagnetic state of the doped fullerene and could be used as a magnetic detector on a molecular scale [183]. Another reason for this development is the vision of a new type of chemistry based on stabilised carbon cages. Endohedral H@C$_{60}$ and exohedral C$_{60}$H$_n$ molecules (where n is an integer equal or less than 60) could have potential applications for hydrogen storage and they have also been suggested as one of the infrared emission sources in interstellar space [184-186].

The fullerene synthesis is very sensitive towards the presence of hydrogen. Formation of C$_{60}$ stops after adding only a few percent of hydrogen to the helium quenching gas. Attempts to hydrogenate C$_{60}$ in the gas phase are unsuccessful because C$_{60}$ is unreactive towards molecular hydrogen [54]. However both the mono-cations and the di-cations of C$_{60}$ and C$_{70}$ can be hydrogenated in the gas phase by reactions with atomic hydrogen yielding C$_{60}$H$_n$ molecules [187]. The dihydride derivative C$_{60}$H$_2$ is formed by the reaction of C$_{60}$ with BH$_3$ tetrahydrofuran in toluene followed by hydrolysis [188]. C$_{60}$H$_{36}$ is a product of

177
Birch reduction [189] and can be generated with transfer hydrogenation as well as [190,191] C$_{60}$H$_{18}$. Brühwiler et al. [192] performed hydrogenation of C$_{60}$ films in a gas phase reaction by exposing the films to atomic hydrogen in vacuum. The hydrogenated films were analysed by a form of secondary ion mass spectrometry (plasma desorption mass spectrometry). Atomic hydrogen was found to be bound covalently to individual fullerene molecules resulting in C$_{60}$H$_n$. $n=2..>=24$ with a wide distribution in $n$ for a given exposure. Evidence for the possible existence of unbonded H within the cage comes from muon experiments with both C$_{60}$ [193] and C$_{70}$ [194]. This work indicates that the muonium can be either free within the cage or bonded externally.

The results of computer simulations [183] concerned with the attempt to implant hydrogen into the C$_{60}$ cage are reported here. The optimum energy for implantation is calculated, but static potential calculations show that it is more favourable for the hydrogen atom to attach on the outside, rather than the inside of the cage. The simulations show that it should be possible to implant H into ‘cold’ C$_{60}$ molecules, but that the probability of a H atom becoming trapped reduces with increased excitation of the molecule, and is small if the internal energy of the C$_{60}$ is above 14 eV. This is confirmed by the experimental investigation which shows that the hydrogen bonds externally to the excited molecules. The trajectories calculated by MD show a number of different interactions: (i) reflection of the H atom, (ii) transmission of the H atom through the structure, (iii) implantation within the molecule, (iv) attachment of the H atom to the outside of the structure and (v) initial implantation and attachment of the H atom to the inside of the structure followed by bond-breaking of the C atoms and final attachment of the H atom externally. The results of simulation agree with those of the experiment and explain the failure to produce H@C$_{60}$ at high temperatures.

8.2 Experimental Details

The experiments described here were carried out by Richter and Mertesacker at the Hahn-Meitner-Institut [183,195] in an attempt to produce endohedral hydrogenated fullerenes by hydrogenation of C$_{60}$ in a hydrogen plasma. Using a plasma provides atomic hydrogen for the reaction and produces energetically excited states of the reacting species. The experiments were carried out by placing pure C$_{60}$ powder in a quartz tube with a high vacuum (i.e. less than 1.33 mPa). The quartz tube was heated to 250 °C in a furnace and then filled with hydrogen gas. At a gas pressure of between 66.66 mPa and 133.32 mPa, a plasma is ignited between a concave cathode and a ‘ring’ anode at a distance of about 20 cm. In the plasma, the molecular hydrogen gas is converted into atomic
hydrogen. The whole plasma system is placed in a furnace and slowly heated to around 550 °C to 600 °C and held at this temperature until the $C_60$ powder is completely sublimated. The experimental setup is illustrated schematically in figure 8.1.

![Figure 8.1. Schematic diagram illustrating the principle experimental set-up for the interaction of $C_60$ with hydrogen plasma.](image)

The plasma properties were estimated by Langmiur probe measurements. The electrons in the low pressure plasma have energies of between 10 eV and 25 eV. These electrons are capable of dissociating and ionising neutral species at high rates at quite a low gas temperature, and therefore of causing a high-temperature chemistry in cold non-equilibrium glow-discharge plasma. The gas phase reactions of these chemically active $C_60$ and hydrogen species are used for endohedral and exohedral hydrogenation of the fullerenes. After interaction with the hydrogen plasma, the sublimated $C_60$ condenses on a water-cooled copper finger at the end of the quartz tube outside the furnace. The $H-C_60$ powder was collected and analysed by various methods.

The condensed powder was first analysed by X-ray diffraction and Raman Spectroscopy in order to ensure that $C_60$ was indeed being produced. The spectra from these experiments were identical to those for pure $C_60$. Further analyses were carried out by using electron spin resonance (ESR) and nuclear magnetic resonance (NMR). If a single $H$ atom were to be trapped at the centre of the molecule, then ESR should indicate both a fullerene line in the spectrum and two additional lines at ± 50 mT, symmetric around the fullerene signal. No evidence
of these signals was obtained. Proton-NMR at 300 MHz shows a broad signal from the $C_{60}$. The signal has a peak at about 6 ppm, characteristic of $C-H$ bonds and at the position corresponding to $C_{60}H_2$.

High performance liquid chromatography (HPLC) experiments were also carried out on the $H-C_{60}$ powder. These indicated the presence of $C_{60}H_2$ and $C_{60}H_4$ in addition to $C_{60}$. The mass spectrum for the $H-C_{60}$ powder shows a strong peak at 720 amu, corresponding to the $C_{60}$ molecule. After allowing for the presence of the $^{13}C$ isotope, the spectrum shows enhancement, relative to pure $C_{60}$ at 721, 722, 723 and 724 atomic mass units. These peaks are therefore interpreted as $C_{60}H_n$, $n=1,..,4$.

The conclusion from the experimental work was therefore that only exohedral $H-C_{60}$ complexes were produced in the plasma, with the number of hydrogen atoms bound to fullerenes lying between zero and four.

8.3 Preliminary calculations

The MD simulations presented here are carried out using empirical many-body potentials. Although the empirical potential models the static energy configurations of small $C-H$ clusters and bulk crystalline carbon well, it is clearly less preferably to use such potentials, than calculate the interactions using ab-initio methods. However, this would be a prohibitively expensive process in terms of computing time for the number of cases considered here. The approximation using empirical potentials should at least enable us to obtain a qualitative if not quantitative view of the dynamic interaction process [195]. The Brenner potential is used as this is the only available potential that deals with $C-H$ interactions. This potential reproduces the optimal structures of small $C$ and $C-H$ molecules, and gives a better description of bond breaking and forming than the Tersoff potential. A comparison of the ability of various potentials to describe the $C_{60}$ structure is given in section 3.8.2. The first parameterisation of the Brenner potential gives a description in good agreement with the reported experimental measurements and ab-initio calculations for the size and structure of the $C_{60}$ cage, and is used throughout this study. Although Brenner’s hydrocarbon potential appears to be the best empirical potential available it does have some drawbacks, notably the $C-C$ interactions cut off after 2.0 Å, the $C-H$ interactions cut off after 1.8 Å and $H-H$ interactions cut off after 1.7 Å. Non-bonded interactions are therefore ignored and there is a region at the centre of the fullerene where no interaction takes place with the hydrogen atom.

The calculations presented here were conducted using the original parameterisation of the potential; since then a modified parameterisation has been
produced that better describes the formation of exohedral fullerene-atom complexes, as described in section 3.8.4. Results of calculations that may be influenced by this modification are indicated and the effects have been investigated. The modification has only a small effect on the calculations performed and the general results are not altered.

Static minimum energy structures of \( C_{60}H \) and \( C_{60}H_2 \) were calculated and a number of these configurations are shown in figures 8.2 and 8.3. For these calculations, the \( H \) atom and adjacent \( C \) atoms were initially placed in approximate positions, and the local minimum energy configuration was found by a steepest descent optimisation method. Bonds are drawn between atoms within the interaction distances of the empirical potential function.

The following local minimum energy structures were calculated for \( C_{60}H \) combinations and are illustrated in figure 8.2.
(a) \( H \) atom externally bonded.
(b) \( H \) atom internally bonded.
(c) \( H \) atom externally bonded, with an adjacent hexagon-hexagon bond broken.
(d) \( H \) atom internally bonded, with an adjacent hexagon-hexagon bond broken.
(e) \( H \) atom externally bonded, with an adjacent hexagon-pentagon bond broken.
(f) \( H \) atom internally bonded, with an adjacent hexagon-pentagon bond broken.

For \( C_{60}H_2 \) combinations, the following structures were optimised and are shown in figure 8.3.
(a) \( H \) atoms externally bonded at opposite ends of the fullerene.
(b) \( H \) atoms externally bonded to adjacent \( C \) atoms on a hexagon-pentagon bond.
(c) \( H \) atoms externally bonded to adjacent \( C \) atoms on a hexagon-hexagon bond.
(d) One \( H \) atom external and one internal, bonded to adjacent \( C \) atoms on a hexagon-pentagon bond.
(e) \( H \) atoms bonded as in (b), but with the bond between the two \( C \) atoms broken.
(f) \( H \) atoms bonded as in (d), but with the bond between the two \( C \) atoms broken.

In the case of a single \( H \) atom interaction with \( C_{60} \), the minimum energy state is for the \( H \) atom to be bound externally to the molecule. From table 8.1 it can be seen that for the \( H \) atom bound outside the structure, the energy is lowered by between 1.6 and 2.35 eV implying that the preferred bonding position is external to the molecule. The energy of an internally bound \( H \) atom is a local minimum, but is predicted to be higher in energy than free \( H \) and isolated \( C_{60} \) using both the unmodified empirical potential and \textit{ab-initio} calculations (the estimate for the value estimated for the modified potential is unreliable due to the
large amount of strain associated with this configuration), although the empirical value appears to be too low. One reason why the calculated energy is not very high when using the empirical potential for this case, is the effect of the short ranged nature of hydrogen interactions. Repulsion between the hydrogen atom and nearby carbon atoms would be expected, and this would raise the energy of the structure. Ab-initio calculations give an energy of around 1.0 eV above that of an isolated fullerene for H@C60 (a H atom trapped, but unbound within C60). This energy cannot be estimated with the empirical potential used in our calculations because the H-C interactions are cut off at distances greater than 1.8 Å, and therefore there is a volume of approximately one eighth of the cage located at the centre of the molecule in which the C-H potential is assumed to be zero. Thus, the empirical potential overpredicts the stability of endohedral complexes by around 1 eV. As interactions between the hydrogen atom and the cage would be expected to increase as the atom approaches the cage, there should be considerable interaction when the hydrogen atom is bound internally. Due to the close proximity of the hydrogen and carbon atoms in this case, the repulsion should be greater than that when the hydrogen atom is unbound and at the of the fullerene. So we can conclude that the omitted long-range C-H interactions would add over 1 eV to the energy of the structure in this case, and would improve the agreement with ab-initio calculations.

Table 8.1. Local potential energy minima calculated for various C60H and C60H2 combinations. The energies quoted are relative to the minimum energy structure of the C60 molecule and an isolated H atom.

<table>
<thead>
<tr>
<th>Structure</th>
<th>C60H Potential (eV)</th>
<th>C60H2 Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
<td>Modified</td>
</tr>
<tr>
<td>(a)</td>
<td>-1.6</td>
<td>-2.35*</td>
</tr>
<tr>
<td>(b)</td>
<td>0.3</td>
<td>-0.45*</td>
</tr>
<tr>
<td>(c)</td>
<td>-0.3</td>
<td>unaltered</td>
</tr>
<tr>
<td>(d)</td>
<td>1.0</td>
<td>unaltered</td>
</tr>
<tr>
<td>(e)</td>
<td>-1.0</td>
<td>unaltered</td>
</tr>
<tr>
<td>(f)</td>
<td>0.6</td>
<td>unaltered</td>
</tr>
</tbody>
</table>

* These values are estimated by assuming the modification would add an extra 0.25 eV to every bond affected. This does not account for the strain induced due to changes in bond lengths and the consequent alteration of bond angles.
† From references [160] and [196].
‡ From reference [197].
Figure 8.2. Local minimum energy structures calculated for $H-C_{60}$ combinations. The dark circles represent the hydrogen atoms, the light circles are carbon.
Figure 8.3. Local minimum energy structures calculated for $H_2$-$C_{60}$ combinations. The dark circles represent the hydrogen atoms, the light circles are carbon.
There is good qualitative agreement between the unmodified empirical potential and \textit{ab-initio} calculations in predicting that the energies of the four states are in order:

\[
E(\text{exo}-C_60H) < E(C_60) < E(H@C_60) < E(\text{endo}-C_60H)
\]

It appears that any \( H \) atom trapped inside the \( C_60 \) would prefer to be located away from an internal bonding position and located near the centre of the cage.

For the \( C_60H_2 \) cases, the results are also summarised in table 8.1. If the \( H \) atoms are bound externally and well-separated, at positions corresponding to that shown in figure 8.3(a) then the potential energy is decreased by 3.3 eV compared to the isolated \( C_60 \) energy (i.e. two times that corresponding to figure 8.2(a). The most stable configuration (-5.9 eV) turned out to be the case where two \( H \) atoms were externally bonded on adjacent \( C \) atoms where the \( C-C \) hexagonal-pentagonal 'single' bond is broken. However MNDO calculations [198] indicate configuration (c) is the preferred minimum energy state for \( C_60H_2 \). The short cut-off distance of the Brenner potential and the approximate method in which bond conjugation is modelled might well be responsible for the erroneous results in the minimum energy structures for \( C_60H_2 \). In the lowest energy case predicted by the empirical potential, strain in the structure forces the two hydrogen atoms close to each other. The minimum energy is achieved when these two atoms are 1.7 Å apart, i.e. just out of interaction distance. Longer ranged interactions in the potential would force these two atoms to be further apart, increasing the strain in the structure. Longer interactions would also mean the associated \( C \) atoms were within interaction distance. Extending the cutoff function by any significant amount would have far reaching consequences on the ability of the potential to model many situations. Such a modification was not attempted as it would necessitate a thorough testing and refitting of the potential and is likely to prevent the modelling of any bulk crystal structures. The potential was therefore used in its original form, but it is noted that the modelling of \( C_60H_2 \) structures is inaccurate. The modified parameterisation described in section 3.8.3 reduces the difference between the energies of \( C_60H_2 \) structures, but does not correct the prediction that case (e) is the lowest energy structure.

The predictions of the original parameterisation of the potential for \( C_60H \) are in reasonable agreement with \textit{ab-initio} calculations, and the rest of this study is concentrated on single atom interactions with the molecule. The initial motivation for this study was the hypothesis that it might be possible to implant a \( H \) atom within the molecule, and so some computer experiments were set up to
examine the feasibility of this by projecting $H$ atoms at different energies towards $C_{60}$ molecules.

Any implantation of the $H$ atom within the structure will require it to traverse an energy barrier and in so doing lose energy itself and impart excitational energy to the $C_{60}$ molecule. The threshold energies for the $H$ atom to cross into the cage were calculated. In these calculations, the $H$ atom was assumed to be incident normally on the centre of one of the hexagonal faces of a $C_{60}$ molecule as this should give the lowest energy path. The fullerene was initially at zero K (i.e. with no internal energy). The energy threshold appears to be around 14 eV. The calculations show that at 13.9 eV, the $H$ atom is repelled by the molecule. At 14.0 and 14.1 eV the $H$ atom binds externally to the molecule and at greater than 14.2 eV, the $H$ atom enters the molecule. Repeating the simulation for escape of a $H$ atom from the centre of the cage gave a similar result. Repulsion from the cage occurred for energies up to 14.1 eV. At 14.2 eV the atom bound to the inside of the cage, at 14.3 eV it bound on the outside of the cage, and for energies of 14.4 eV and over the $H$ atom escaped. The available *ab-initio* value for this barrier is 3.8 eV [196], but is based on a static calculation where the fullerene was allowed to relax as a hydrogen atom moved through a hexagonal face. The large difference in the results is due to the energy that would have to be imparted to the cage by the incoming $H$ atom to cause that relaxation in the dynamical calculation. To allow a good comparison between the calculations, the static potential energy was calculated using the Brenner potential. The distance from the $H$ atom to the centre of the face was varied and the energy of the system was minimised for each separation. The resulting energy profile is shown in figure 8.4. It can be seen that the potential energy increases by 3.9 eV when the particle is located at the centre of the relaxed hexagonal ring, in very good agreement with the *ab-initio* calculations.
Figure 8.4. The static potential energy calculations for a H atom passing through the centre of a hexagonal face from outside to inside the molecule.

8.4 Interactions with a ‘cold’ C60 lattice

C60 molecules condense to form a face-centred cubic (fcc) structure known as fullerite. This has a cell edge of 14.1 Å and a nearest neighbour spacing of 10.0 Å [165]. MD simulations were conducted to find the optimum energy for implanting H atoms in the surface layer of this structure. To increase the efficiency of the simulations, only three neighbours in the surface layer of the lattice were modelled and it was assumed that the incoming H atoms were incident normally on an irreducible symmetry zone of the surface layer. The three fullerenes and the symmetry zone are shown schematically in figure 8.5.

The fullerenes were assumed to have no internal energy at the start of the simulation, but were randomly oriented with respect to each other. This orientation was altered before the start of each trajectory and the impact point was also randomly selected. A total of 500 simulations were run at each of 12 different hydrogen atom energies between 11 and 44 eV. For the purpose of generating the statistics, the simulations were run until the H atom had entirely escaped from the system or for 1 ps.
Figure 8.5. The irreducible symmetry zone for the fcc fullerite surface, depicted by the triangle. The molecules are labelled 1, 2 and 3, consistent with the nomenclature used in Table 8.2 and Figure 8.6.

The results are shown in Table 8.2 and plotted in Figure 8.6. It can be seen that there is some implantation for particles with initial energy of 14 eV or more but that the preferred energy for implantation is 23 eV, where nearly 5% of the H atoms are predicted to implant and stay within the molecules for excess of 1 ps. This is an average over the total representative area, but only around 60% of the incident atoms can be expected to have a direct collision with the fullerene. If it is assumed that all atoms trapped in molecule 1 are the result of direct collisions, the proportion of direct impacts leading to capture is approximately 8% for the 23 eV trajectories. None of the cases where the hydrogen atom was predicted to be trapped involved bonding between the cage and the atom. It can also be seen that not all atoms implant into molecule 1. There are a number of H atoms which reflect off molecule 1 but end up being trapped by molecules 2 and 3. Trapping in these molecules is a maximum for energies between 26 eV and 32 eV. This is presumably because the atom loses some energy during the initial collision with molecule 1, and then approaches molecule 2 or molecule 3 with an energy close to 23 eV. Very few atoms were observed to become bound to the outside of the fullerene and although the majority of exohedral structures occur at energies above 26 eV, there is no identifiable trend to their formation. There is also the possibility that atoms with a low energy can directly bond to the outside of the molecule without first penetrating the cage, as indicated by the atom with a kinetic energy of 11 eV binding to the cage. For those atoms that are not trapped, the numbers backscattered and passed through the layer are indicated. As expected as the energy increases, the backscattering reduces and transmission straight through increases.
Table 8.2. Implantation results for $^1$H atoms incident on the first layer of a fullerite lattice at zero K. 500 trajectories were simulated at each of the 12 incident energies.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Back-scattered</th>
<th>Total inside</th>
<th>Number in 1</th>
<th>Number in 2</th>
<th>Number in 3</th>
<th>Total outside</th>
<th>Passed through</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0</td>
<td>214</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>285</td>
</tr>
<tr>
<td>14.0</td>
<td>197</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>299</td>
</tr>
<tr>
<td>17.0</td>
<td>185</td>
<td>11</td>
<td>9</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>302</td>
</tr>
<tr>
<td>20.0</td>
<td>136</td>
<td>21</td>
<td>14</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>343</td>
</tr>
<tr>
<td>23.0</td>
<td>139</td>
<td>24</td>
<td>18</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>338</td>
</tr>
<tr>
<td>26.0</td>
<td>126</td>
<td>19</td>
<td>11</td>
<td>7</td>
<td>1</td>
<td>5</td>
<td>350</td>
</tr>
<tr>
<td>29.0</td>
<td>117</td>
<td>16</td>
<td>11</td>
<td>4</td>
<td>1</td>
<td>5</td>
<td>362</td>
</tr>
<tr>
<td>32.0</td>
<td>106</td>
<td>16</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>9</td>
<td>369</td>
</tr>
<tr>
<td>35.0</td>
<td>79</td>
<td>16</td>
<td>11</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>405</td>
</tr>
<tr>
<td>38.0</td>
<td>88</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>0</td>
<td>7</td>
<td>400</td>
</tr>
<tr>
<td>41.0</td>
<td>96</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>397</td>
</tr>
<tr>
<td>44.0</td>
<td>90</td>
<td>5</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>402</td>
</tr>
</tbody>
</table>

Figure 8.6. The number of atoms trapped in, or bound to the molecules as a function of the initial energy.
Some special cases of $H$-$C_60$ interaction were also analysed where the trajectories were continued for longer than 1 ps. In these cases the final equilibrium configuration is only reached after times of the order of a few picoseconds. Figure 8.7 shows various stages in one especially interesting interaction of a 20 eV $H$ atom with a $C_60$ molecule for times up to 3.8 ps. The interesting point about this trajectory is that although the $H$ atom initially implants, it eventually attaches to the outside of the molecule. The $H$ atom is initially incident on the pentagonal face at 15° to the normal and penetrates the fullerene cage. The atom becomes trapped within the molecule, but interactions lead to the breaking of a $C-C$ bond after about 23 fs. In all the simulations conducted where a bond breaks, it has been the weaker bond between the hexagonal and pentagonal faces that has broken. After the bond has broken, the $H$ atom is adjacent to an undercoordinated $C$ atom and attaches to it. At a later time the broken $C-C$ bond reforms but the other hexagonal-pentagonal bond on the atom breaks. As it does so the $C-H$ bond flips to the outside of the cage. The molecule vibrates for a considerable amount of time until finally after about 3.8 ps the $C-C$ bond reforms. The long time taken for this bond to reform is partly due to the short range of the potential, that prevents the two $C$ atoms on the broken bond from interacting. The final state of the attached $H$ atom is equivalent to the minimum energy structure shown in figure 8.2(a). This final externally bonded state took one of the longest times to achieve of any of the simulations run but illustrates the point that if a $H$ atom is initially bonded internally to a $C_60$ molecule then this bond can easily switch to an external bond. Examples of all the various cases have been animated and a computer video depicting these events has been produced [81]. The values for the minimum energy structures given in table 8.1 for the $C_60H$ system indicate that there could be a smaller energy barrier for the $H$ atom to leave the centre of fullerene by the mechanism illustrated in figure 8.7 than by simply passing though the centre of a hexagonal face. This remains to be checked by ab-initio calculations, as energy barriers predicted by empirical potentials are known to be unreliable [156,157].

Figure 8.8 shows the energy change of the $H$ atom and $C_60$ molecule for a trajectory where the $H$ atom is predicted to implant within the structure. The excess potential energy (i.e. above the equilibrium state for an isolated $H$ atom and cold $C_60$ molecule) and the kinetic energy is plotted as a function of time for a $H$ atom with an initial kinetic energy of 22 eV.
Figure 8.7. Various stages in the interaction of a H atom with 'cold' C$_{60}$. The H atom is projected towards the centre of the pentagonal face at an angle of 15° to the normal with an initial kinetic energy of 20 eV.
Figure 8.8. The potential and kinetic energy changes plotted as a function of time for the case where a 22 eV $H$ atom is trapped within the molecule. $H$ denotes the hydrogen atom and BF is the buckminsterfullerene molecule.

The $H$ atom enters the fullerene and once inside it collides with the inside of the cage approximately every 13 fs. During each collision, the atom loses around 20% of its kinetic energy to the fullerene, resulting in a roughly exponential decay. The energy of the $H$ atom rapidly decreases below the 14 eV threshold calculated for escape from the molecule through the centre of a face. After 0.5 ps the kinetic and potential energy of the $H$ atom is almost zero. The $H$ atom now spends a lot of time near the centre of the molecule where the $C-H$ potential does not model any interaction. The kinetic and potential energy transferred to the fullerene equilibrates rapidly, reaching a quasi-steady state after about 300 fs. Figure 8.9 shows a simulation with similar initial conditions, except the $H$ atom has an initial energy of only 14 eV. The $H$ atom never enters the fullerene, but bonds to the outside of the structure, losing most of its kinetic energy within 7 fs.
Figure 8.9. The potential and kinetic energy changes plotted as a function of time for the case where a 14 eV H atom becomes externally bonded to the molecule.

Figure 8.10 is for a 24 eV H atom which passes through the molecule. In this case, the interaction is over within 25 fs, with 16 eV being transferred to the molecule. The portions of the trajectory where the atom passes through the cage are clearly visible as much of its kinetic energy is lost as the cage is deformed and then regained as the displaced C atoms relax back. It can be seen that as in figure 8.9, rapid equilibration between potential and kinetic energy within the molecule takes place.

The evidence from table 8.2 and the above detailed trajectories shows that it should be possible for a H particle to implant within an initially cold C\textsubscript{60} structure and to transfer its kinetic energy by collisions with the C atoms until it has insufficient energy to escape from the cage. This suggests that a possible technique for producing H implanted C\textsubscript{60} is to bombard the fcc fullerene lattice at normal incidence at the optimum energy for implantation and then to remove the material layer by layer after sufficiently large H doses. It would then be necessary to strip off any H attached to the outside of the molecule, which being externally bonded would be more amenable to chemical reaction than the internally implanted H.
Figure 8.10. The potential and kinetic energy changes plotted as a function of time for the case where a 24 eV H atom passes through the molecule.

8.5 Interactions with 'heated' C₆₀

The experimental attempts to produce H@C₆₀ were not of the form described in section 8.4, but involved sublimated C₆₀ molecules passed through a H plasma. The fullerenes are sublimated at a temperature between 550 °C and 600 °C, and the mean energy of the plasma is estimated to be around 25 eV. The ions within the plasma will transfer energy through collision with C₆₀ molecules as the molecules pass through the plasma. Since the collision process occurs primarily with a single C atom of the C₆₀ structure, it is possible for the molecule itself to have a total internal vibrational energy in excess of 25 eV.

Simulations were run of H interaction with C₆₀s which had internal energies of 14 eV and 33 eV, i.e. corresponding to the estimated sublimation temperature and slightly greater than the estimated mean ion energy. These energies are equivalent to temperatures of approximately 630 °C and 1850 °C. The initial kinetic energy of the H atoms was always equal to the mean ion energy of 25 eV. Simulations were also run for internal energies of 52 eV (3080 °C), 71 eV
(4300 °C) and 90 eV (5530 °C) to study the effects of higher plasma temperatures. A total of 200 trajectories were run at each internal energy of the fullerene.

A system consisting of a single H atom and an isolated energetic C₆₀ molecule was studied in the MD simulations. To introduce the energy into the C₆₀ molecule one sixtieth of the total energy required to be added was given to each C atom with the velocity in a random direction. The C₆₀ was allowed to equilibrate for 1 ps, then randomly oriented before the H atom was introduced into the simulation. Using this method, the added energy is mainly in the form of internal vibrational energy rather than rotational or linear kinetic energy of the molecule as a whole. The H atom is now assumed to be incident over the region given by the quarter circle centred on the C₆₀ molecule shown in figure 8.11, and projected downwards.

![Figure 8.11. The impact zone for H interactions with the 'energetic' C₆₀ molecules. The centre of mass of the molecule is the centre of the circle.](image)

The simulations were run for 8 ps or until the H atom escaped from the system. Inelastic energy losses were ignored and the system is Hamiltonian in form, so energy is conserved. If the H atom was trapped in, or bound to, the fullerene after 8 ps, the simulation was continued for a further 1 ps with an energy loss scheme applied to allow the system to achieve an equilibrium state. The final state of the system was visually checked to determine the outcome of the simulation.

For the 14 eV internal energy case, it was found that 5 of the 200 incident H atoms became trapped within the molecule. However 14 formed external bonds but maintained the C₆₀ structure. A further H atom bonded in such a way as to cause a breaking of one of the hexagonal-pentagonal bonds and one H bonded but caused multiple bond-breaking in the molecule. At 33 eV no H atom implanted within the molecule although one out of 200 bonded on the inside of the cage, 4
bonded externally with no broken bonds, 2 with single bonds broken and 7 with multiple bond breaking.

Figures 8.12 and 8.13 illustrate time sequences of the interaction of a single $H$ atom projected vertically downwards with 25 eV energy towards molecules with internal energies of 14 and 33 eV respectively. In these diagrams we draw bonds between the circles representing the atoms if the atoms are within the interaction distance of the potential function (2.0 Å for C-C and 1.8 Å for C-H). The times given are from the first interaction between the atom and the fullerene.

These time sequences illustrate the predominant case where the $H$ atom initially implants but eventually becomes bound to the outside of the molecule. In all cases the broken C-C bonds were those between hexagonal and pentagonal faces, i.e. the longer ‘single’ bonds. Figure 8.12 shows that even for an initial internal energy of 14 eV there is severe distortion to the structure due to the transfer of energy from the $H$ atom. However the bonds of the fullerene eventually reform after the interaction. At an initial internal energy of 33 eV (figure 8.13) the bonds constantly break and reform. However when the simulation is continued for longer times there is insufficient internal energy for any atom to become detached from the cluster. In both cases the $H$ atom becomes bound to the outside of the molecule after similar time scales.

For the cases where the initial energy of the fullerene was 52 eV or above, a large amount of damage occurred to the molecule. 19 $H$ atoms remained bound to fullerenes with 52 eV internal energy, but in all cases several C-C bonds were broken and the molecule was severely damaged. Interactions with 71 eV fullerenes resulted in 11 cases of the $H$ atom remaining bound to the molecule, but the fullerene was either severely damaged or lost its cage structure completely. The fullerene with 90 eV internal energy was always destroyed, with the molecule fragmenting in the 13 cases where a $H$ atom remained bound to a C atom. Simulations of an isolated fullerene with an internal energy of 90 eV showed that it was stable on the timescale simulated here. The energy gained from the $H$ atom, coupled with the loss of symmetry and increased strain in the cage due to the $H$ atom binding to the cage is probably responsible for the rapid disintegration of the molecule.
Figure 8.12. The interaction of a H atom with an initial kinetic energy of 25 eV and a C$_{60}$ molecule with an initial internal energy of 14 eV.
Figure 8.13. The interaction of a $H$ atom with an initial kinetic energy of 25 eV and a $C_{60}$ molecule with an initial internal energy of 33 eV.
8.6 Conclusions

The experimental results showed no evidence of a single $H$ atom located at the centre of the $C_{60}$ molecule. Since this would be a paramagnetic state it would be easily detected in ESR even in small quantities. The explanation presented here is that the excitation of the $C_{60}$ molecule as it passes through the plasma prevents the formation of this state as indicated in the 'warm' molecule simulations carried out.

The calculated static potential energy configurations analysed seem to indicate that $C_{60}H_2$, where the $H$ atoms are attached to adjacent C atoms from a broken hexagonal-pentagonal bond is one of the preferred minimum energy states with a potential energy of 5.9 eV less than that of the isolated $C_{60}$ molecule. The prediction that a broken bond exists in the lowest energy structure is clearly an artifact resulting from the short-ranged nature of the empirical potential. The results of ab-initio calculations show that the addition of two $H$ atoms at opposite ends of a 'double' bond is the preferred structure [198]. Further $H$ atoms added in pairs at other similar but separated bonding sites on the molecule would be expected to reduce the potential energy further by similar amounts. These might well be the most common structures for $C_{60}H_4$ and $C_{60}H_6$. However the addition of further atoms would also increase the strain energy of the cage (figure 8.3(a) shows a considerable strain to the molecule) and it is known that $C_{60}H_4$ and $C_{60}H_6$ decompose over long time whereas $C_{60}H_2$ is stable. The addition of internally bonded $H$ atoms within the cage could stabilise $C_{60}H_n$ molecules and has recently been considered [199].

The results of the MD simulations lead to the conclusion that the collision of $H$ atoms with energetic $C_{60}$ molecules leads to chemical bonding and the formation of exohedral structures. This is consistent with the results of experiment, where exohedral complexes with up to four hydrogen atoms were detected. Simultaneous interaction of more than one hydrogen atom with a $C_{60}$ has not been considered by simulation, as the description of $C_{60}H_2$ systems by the empirical potential shows qualitative and quantitative disagreement with ab-initio calculations. The conclusion of ab-initio calculations is that two externally bonded $H$ atoms is a potentially favoured state which does not cause too much distortion to the $C_{60}$ cage. Once one exohedrally bound hydrogen exists, the addition of a second at the other end of the 'short' hexagon-hexagon bond [197] is likely as a radical orbital exists.

The difficulty in forcing the $H$ atom to implant at the centre of the cage has led to the proposition of two possible experiments by which this might be
achieved. One such possibility would be to bombard a fullerite lattice. The main experimental difficulty would appear to be how to do this without imparting too much energy to the molecule since it would appear that it is more difficult both to implant and to contain the $H$ atom within the vibrating $C_{60}$ structure. One possibility might be by producing a Langmuir-Blodgett film of $C_{60}$ and irradiating with a low dose, low energy proton beam. Such experiments have yet to be conducted.
Chapter 9

Summary, Conclusions and Future Work

9.1 Summary and Conclusions

In this thesis several different features of carbon based materials have been studied by computer simulations based on the classical molecular dynamics technique. The description of complex, multicomponent systems has been successfully achieved using combinations of empirical potential functions. It has been shown that many-body potentials provide sufficient accuracy to describe many processes important to the behaviour of carbon and silicon systems.

The resilience of $C_{60}$ whilst undergoing collision with silicon crystal surfaces has been demonstrated. At impact energies of up to 250 eV, the fullerene maintains its structure, although bonds can occasionally be broken within the cage. Depending upon the impact energy and the angle of incidence, the fullerene can scatter from bare and hydrogen terminated surfaces. Reflection usually occurs at incidence angles that are near grazing, with energies between 100 eV and 250 eV. In some circumstances the fullerene can be reflected, but pull atoms from the surface. Interaction with bare silicon rarely results in scattering due to the dangling bonds on the silicon surface. Hydrogen termination does not prevent reaction; the large momentum of $C_{60}$ knocks surface hydrogen atoms into interstitial positions, thus allowing reaction between the fullerene and the exposed surface silicon atoms. Normal incidence at 1 keV on the bare silicon surface produces a region of disordered $Si$ and $C$ atoms that extends around 10 Å into the surface. It is suggested that this process could be useful in the formation of thin $SiC-Si$ interfaces. The sputtering yield due to 5 keV fullerene bombardment of silicon is an order of magnitude higher than single ion bombardment at the same energy as most of the impact energy is transferred to the surface layers of the target. The highest yield occurs at incidence angles of around 40° to normal, in contrast to the maximum yield for ion bombardment which occurs at approximately 60° to normal.

The low energy deposition of fullerenes on a silicon substrate has also been investigated by MD. By using a combination of many-body and long-ranged potential functions, the interaction of $C_{60}$ with the silicon surface and the growth of multilayer films can be accurately modelled. This has enabled the effect of
substrate temperature on the nature of film grown to be investigated. Both cubic and hexagonal stacking are found to be stable in the first monolayer. The stability of the cubic phase is increased at low temperature (less than 300 K). Higher temperature causes the fullerenes to be more mobile on the surface, this allows them to escape from the minimum energy positions of isolated fullerenes and achieve a nearest neighbour separation closer to that of bulk fullerite.

The phenomenon of bump formation on ion bombarded graphite has been examined. The process appears to be caused by a carbon self interstitial between surface graphite layers. The interstitial is formed from a carbon atom knocked out of its position in one of the surface layers. As the bump is caused by an interstitial carbon atom, the nature of the bump is relatively insensitive to the bombarding ion used. The inclusion of interlayer forces for graphite in the model of the system does not change the description of the processes leading to bump formation. The neglect of interlayer terms has also been shown to have little effect on the description of the behaviour of graphite under 500 eV fullerene bombardment for timescales less than 10s of picoseconds. For these timescales and energies, the dynamics are dominated by the strain caused by distortion of the graphite planes, during. Calculations of the displacement threshold energy for an atom in the graphite lattice gives a value of around 34 eV, this is in excellent agreement with recent experimental predictions.

Simulations of ion bombardment of polyethylene have shown that the initial stages of ion bombardment can be modelled by short-ranged potentials. The bombardment of a polyethylene crystal by 1 keV Ar atoms causes chain breaking and the ejection of atoms, radicals and small molecules. Many fragments caused by the initial collision recombine in the surface layers of the target before escaping into the gas-phase. The ejection of hydrogen atoms and molecules leads to carbonisation of the target. The complete trajectory of a 1 keV Ar bombardment will last for several picoseconds. The addition of long-ranged interaction potentials is essential if simulations are to be run for times of this scale, as the energies in parts of the target will become low enough that non-bonded interactions are important. Long-ranged potentials have been developed, but at present their use is limited due to the computational resources required for their evaluation.

The usefulness of conducting realistic simulations that are directly related to aspects of current experimental investigations has been shown. MD simulations of the interaction of atomic hydrogen with $C_{60}$ were able to verify and explain the results of experiment and led to suggestions for possible future experiments. Experiments were conducted in an attempt to produce endohedral $H@C_{60}$, but only exohedral $C_{60}H_n$ complexes were formed. The conclusions obtained from
simulation were that it is possible to implant hydrogen atoms into $C_{60}$ molecules, but that the energy imparted to the fullerene in producing the endohedral molecule is sufficient to cause reaction. The reaction sequence most commonly observed was where the $H$ atom first became bound to the inside of the fullerene cage. The strain that exists in this structure then leads to the breaking of one of the 'single' hexagon-pentagon bonds on the four-fold coordinated atom. Once the cage is damaged, the $C-H$ bond is able to flip to the outside of the cage and the cage structure is then restored. As the reactivity of the fullerene increases with temperature, it is suggested that a possible method of producing $H@C_{60}$ would be by low energy proton bombardment of a fullerite film.

The simulation of systems consisting of a number of differing elements can be made possible by combining existing potential functions. In particular, the ease with which potential functions based on the Tersoff formalism can be joined together has been illustrated in the case of $C/Si/H$ interactions. This potential was used to model fullerene interactions with bulk silicon. Due to the fitting of the potentials used in its construction, this new potential can describe bulk carbon, silicon and silicon carbide as well as gas-phase hydrocarbon and hydrosilicon molecules. The description of mixed $C-Si-H$ molecules has been examined and is satisfactory. However, certain aspects of the potential, especially those involving undercoordinated silicon atoms, could be significantly improved by refitting some parameters and the addition of correction terms to account for non-local effects.

Long-ranged potentials have been developed, for use in conjunction with short-ranged many-body potentials. These potentials model non-bonded interactions in carbon based materials in an approximate manner, whilst allowing bond breaking and bond formation to occur. While these potentials give the correct structure and binding energy for undisturbed solids, they do have unwanted features. Because the potentials do not take the local environment of atoms into account, they introduce artifacts at separations between the equilibrium distance for non-bonded interactions and the interaction distances described by short-ranged potentials. The proposed way to correct for this is to include a function to account for the local environment of atoms involved in non-bonded interactions. Current workstation sized computers are not sufficiently powerful to calculate vast numbers of long-range interactions, so there is a need to develop efficient algorithms to allow non-bonded interactions to be described with the minimum of calculation.

An new molecular dynamics code that is optimised for use on single workstations has been developed. The code has been shown to be highly efficient and portable and has been chosen for use by several research groups. Techniques for the production of computer generated animation have been developed. The
production methods are based on freely available public domain software. The efficient production of high quality movies has been useful both as a method of gaining understanding of dynamical processes and as a way of communicating results to others.

9.2 Ongoing and Future Work

In this thesis, several different types of ion and molecular bombardment of covalent materials have been investigated. There exist many more surface bombardment problems where investigation by MD is necessary. Some of these problems are already being addressed, while others have yet to be attempted.

Experimental investigation of the energetic interaction of $C_{60}$ and other fullerenes with graphite surfaces has now produced a considerable amount of data. Information on the relationship between fullerene energy and crater depth [200]. Bumps, similar to those produced by ion bombardment have also been observed to be formed on the graphite surface. MD simulation using the code presented in chapter two has been started at The University of Surrey to investigate the processes occurring during the $C_{60}$-graphite interactions.

The ion bombardment of fullerite has also begun to be studied experimentally [201], and MD simulations have been started at Loughborough University. The preliminary results these simulations suggest that 1 keV $Ar$ bombardment causes localised damage to the surface of the crystal, and polymerisation of the fullerenes to form a network of cross linked cages with the majority of the carbon atoms remaining $sp^2$ hybridised. Further detailed study of the bombardment processes is currently being conducted to ascertain the size and stability of these polymer units and to investigate the relationship between ion type and energy and the resulting damage to the fullerite structure.

The processes that are responsible for the formation of fullerenes are still not fully understood. Hypotheses for the formation process range from the atom by atom growth of the cage [35], or condensation of benzene-like hexagon fragments [202], to wrapping of long carbon chains [203], or the rolling up of large faulted graphite fragments [204]. Work recently initiated at Loughborough has resulted in the simulation of the condensation of atomic carbon to a spheroidal fullerene, where every atom is threefold coordinated [205]. This was achieved by employing a more stochastic model than those usually used for such simulations. In this new work, a carbon gas of between 60 and 120 carbon atoms is enclosed small region of space (a cube with sides of approximately 50 Å), with periodic boundary conditions applied in all directions. Also included are around 30 noble gas (either argon or helium) atoms that are weakly coupled to a thermal bath with
a temperature of 2000 K to 3000 K. The temperature of the system is initially several thousand K, and the only way that the carbon atoms can loose energy is via collision with the noble gas atoms. The reaction sequence is shown in figure 9.1, and starts with atoms coalescing to form dimers and trimers. As energy was slowly dissipated from the system, longer chains formed. Once the length of chains began to exceed around 10 atoms, monocyclic rings appeared. The continued coalescence of chain and ring fragments leads to the formation of single rings containing up to 80 atoms. These rings are maintained for a considerable timescale, but eventually two portions of the ring come together and bond to form threefold coordinated atoms. The energy released as these bonds are formed causes the rest of the ring to rapidly wrap round the newly bonded region. Hence a highly faulted cage structure is formed. The great amount of energy released due to formation of many bonds gives the cluster a high temperature and annealing processes can occur. The cluster stays near its melting temperature (about 5000 K) and annealing occurs via multiple bond breaking and formation as well as the ejection and capture of carbon atoms and small molecules. A simulation time of around 2 ns is required for the formation of an unfaulted fullerene. The formation process is highly dependent upon the ratio of carbon to noble gas atoms and the strength of coupling between the noble gas atoms and the thermal bath. This work is now being continued to reproduce the experimental conditions as closely as possible and to find the optimum bath temperature, time constant and ratio of carbon to noble gas atoms.

The many possible applications of fullerenes and related compounds also makes them good candidates for study. The formation of diamond like carbon by compression of fullerite [206-208], and the growth of pure and doped fullerene films on semiconductor and metal surfaces are all processes in need of examination by MD simulation. The use of fullerene bombardment of silicon, with annealing to produce thin SiC-Si interfaces has also been suggested and is suitable for investigation by MD. Ab-initio calculations suggest the double fullerene C$_{60}$@Si$_{60}$ shown in figure 9.2, and consisting of a C$_{60}$ fullerene inside a Si$_{60}$ fullerene, will be stable [209]. Experimental attempts to produce (SiC)$_{60}$ by CVD of silicon onto C$_{60}$ are now being initiated [210], and classical MD simulation will be a useful method of examining any growth processes. The empirical potential introduced in section 3.4.6 can describe the CVD process, although some refitting of the parameters may be necessary to increase the accuracy of the description.
Figure 9.1. Snapshots during fullerene formation. The system consisted of 120 carbon atoms and 30 argon atoms and was initially at 5000 K. The argon atoms were coupled to a 2000 K Berendsen bath with a time constant of 1 ps.
Figure 9.2. The hypothetical double fullerene $C_{60}@Si_{60}$. The molecule consists of a carbon fullerene inside a silicon fullerene and has icosahedral symmetry.

The ability to generate data by *ab initio* calculation makes it possible to fit empirical potentials to describe and study materials such as cubic boron nitride and carbon nitride. These new materials have been predicted to have exceptional physical properties. Large scale MD simulation could be a way of examining these predictions and methods for their production. Attempts are currently being made to fit a Tersoff-type potential for $B/N$ alloys using *ab-initio* calculations to provide the necessary fitting data [124].
References

[26] Using the CM-5 at Los Alamos National Laboratory - N.G. Jensen, (Private Communication)
[51] T. Thundat, R.J. Warmack, D. Ding & R.N. Compton,
[56] A.N. Barrett & A.L. Mackay, Spatial Structure and the Microcomputer
[67] J.M. Haile, Molecular Dynamics Simulation : Elementary Methods
(John Wiley, New York, 1992)
[70] M. Sayed, Computer Simulations of Atomic Displacements and
Recovery Processes Induced by Ion Bombardment in Semiconductors,
[71] L.A. Marqués, J.E. Rubio, M. Jaraíz, L. Enríquez & J. Barbolla,
[81] K. Beardmore & R. Smith, Interaction of C60 with bare and H terminated Si surfaces video, Department of Mathematical Sciences, Loughborough University, UK. (1995)
[83] Present URL is:
http://info.lut.ac.uk/departments/ma/Research/MolecularDynamics/index.html
[84] Rayshade, by C.E. Colb,
http://www-graphics.stanford.edu/~cek/rayshade/rayshade.html
[85] Independent JPEG Group, ftp://ftp.uu.net/graphics/jpeg
[87] Berkeley MPEG-1 Video Encoder & Decoder,
http://www-plateau.cs.berkeley.edu/mpeg
[88] Parallax Graphics Inc., 2500 Condensa St., Santa Clara, CA 95051

[211]
[114] D.G. Pettifor, CCP5 Annual meeting, Daresbury Laboratory, 20th-22nd September 1995
[123] W. Eckstein, Computer simulations of Ion-Solid interactions
       (Springer-Verlag, Berlin, 1991)
[124] K. Albe & K.-H. Heinig, CCP5 Annual meeting, Daresbury Laboratory,
       20th-22nd September 1995
[127] D.W. Brenner (Private Communication)
[129] Y. Chabal, G.S. Higashi, K. Raghavachari & V.A Burrows,
[133] A.J. Dyson (Private Communication)
[135] K.P. Huber & G. Herzberg, Constants of Diatomic Molecules
       (Reinhold, New York, 1979)
       (Wiley, New York, 1989)
[140] NBS Tables of Chemical Thermodynamic Properties,
[141] J.D. Goddard, Y. Yoshioka & H.F. Schaefer,
[142] Fiche F.35. - part B. The Voronoi Construction in 3D,
       CCP5 Program Library, Daresbury.
[144] J.F. Ziegler, J.P. Biersack & U. Littmark,
       The Stopping and Range of Ions in Solids, (Pergamon, New York, 1985)
[147] J. Cornish, V.C.A. Hanrauty & D.A. Morton-Blake,
[160] C.D. Latham (Private Communication)
      (Gordon and Breach Science Publishers, New York, 1986)
      C.A. Evans, K.D. McKeegan, H.A. Storms & H.W. Werner
      (John Wiley & Sons, Chichester, 1990)
[183] K. Beardmore, R. Smith, A. Richter & B. Mertesacker,
[186] S. Petrie, G. Javahery, J. Wang & D.K. Bohme,
[188] R.E. Haufler, J. Conceicao, L.P.F. Chibante, Y. Chai, N.E. Byrne,
      M.A. Ciufolini, R. Hauge, J.L. Margrave, L.J. Wilson,
[189] L. Leserman, G. Degols, P. Machy, J.P. Lonetti, N. Mecht & B. Lebleu,
      in: Prospects for Antisense Nucleic Acid Therapy of Cancer & Aids,
[190] C. Ritchardt, M. Gerst, J. Ebenhoch, D.D. Beckhaus,
      E.E.B. Campbell, R. Tellgmann, H. Schwarz, T. Weiske & S. Pitter,
      Angew. Chem., 105, 609 (1993)
[192] P.A. Brühwiler, S. Anderson, M. Dippel, N. Martensson,
[194] Ch. Niedermayer, I.D. Reid, E. Rodimer, E.J. Ansaldo, C. Bernhard,
U. Binniger, H. Glückler, E. Recknagel, J.T. Budnick & A. Weidinger,

[195] K. Beardmore, R. Smith, A. Richter & B. Mertesacker,
Vacuum, 46, 1091 (1995)


[197] M. I. Heggie, R. Jones & P.R. Briddon, unpublished

[198] C.C. Henderson, C.M. Rohlfing & P.A. Cahill,


[200] G. Bräuchle, S. Richard-Schneider, D. Illig, J. Rockenberger,

[201] O. Gibson, Dartmouth College (Private Communication)


[203] J.M. Hunter, J.L. Fye, E.J. Roskamp, M.F. Jarrold,

[204] D.H. Robertson, D.W. Brenner & C.T. White,

[205] R. Smith & K. Beardmore, CCP5 Annual meeting,
Daresbury Laboratory, 20th-22nd September 1995


[209] S. Ōsawa, M. Harada & E. Ōsawa,

[210] E. Ōsawa (Private Communication)