Modelling Of Energetic Molecule-Surface Interactions

M. Kerford

Submitted for the Degree of Doctor of Philosophy from the University of Surrey

Unis

SCRIBA, University of Surrey
School of Electronic Engineering, Information Technology and Mathematics
University of Surrey
Guildford, Surrey GU2 7XH, U.K.

September 2000

© M. Kerford 2000
Abstract

This thesis contains the results of molecular dynamics simulations of molecule-surface interactions, looking particularly at fullerene molecules and carbon surfaces. Energetic impacts of fullerene molecules on graphite create defect craters. The relationship between the parameters of the impacting molecule and the parameters of the crater are examined and found to be a function of the energy and velocity of the impacting molecule. Less energetic fullerene molecules can be scattered from a graphite surface and the partitioning of energy after a scattering event is investigated. It is found that a large fraction of the kinetic energy retained after impact is translational energy, with a small fraction of rotational energy and a number of vibrational modes.

At impact energies where the surface is not broken and at normal incidence, surface waves are seen to occur. These waves are used to develop a method of desorbing molecules from a graphite surface without damage to either the surface or the molecules being desorbed. A number of fullerene molecules are investigated and ways to increase the desorption yield are examined. It is found that this is a successful technique for desorbing large numbers of intact molecules from graphite. This technique could be used for desorbing intact molecules into a gas phase for mass spectrometric analysis.

Key words: Molecular Dynamics, Fullerene, Carbon, Desorption, Scattering
Acknowledgements

There are many people to thank for the help I have received over the duration of this study. To anyone who has contributed I wish to extend my thanks. There are a number of people without whom I would not have reached this stage.

I wish to thank the Engineering and Physical Sciences Research Council for their funding and support, and the University of Surrey for providing the opportunity to carry this research. Many thanks must go to my supervisor, Dr. Roger Webb, whose guidance and encouragement has enabled me to learn so much. I should like to express my gratitude to Bevis King and the computing support staff for keeping our computers alive when I needed them. I wish to thank Dr. Keith Beardmore, whose simulation code provided me with the basis of this research, for encouragement and many fruitful discussions.

Finally my thanks go to my friends and family who have supported me throughout. Without my husband Steve I would not have been able to maintain my enthusiasm and quest for learning.
# Contents

<table>
<thead>
<tr>
<th>Contents</th>
<th>vi</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>vii</td>
</tr>
</tbody>
</table>

## 1 Introduction

1.1 Motivation ................................................. 1

1.2 Objectives .................................................... 3

1.3 Novel Contributions and Achievements ................. 3

## 2 Background

2.1 Applications .................................................. 9

2.1.1 Particle - Surface Interactions ....................... 9

2.1.2 Cluster Projectiles ....................................... 13

2.1.3 Desorption ................................................. 15

2.1.4 Scattering .................................................. 18

2.2 Mathematical Modelling ..................................... 19

2.2.1 Analytical Models ......................................... 20

2.2.2 Binary Collision Models .................................. 21

2.2.3 Multiple Interaction Model .............................. 24

2.2.4 Potentials ................................................. 28

## 3 Method

3.1 Simulation .................................................... 33

3.1.1 Description of Program ................................... 34

3.1.2 Desorption Layers ......................................... 41

3.2 Analysis ....................................................... 42

3.2.1 Energy Transfer ............................................ 42
| Contents |
|---------------------------------|-----|
| 3.2.1.1 Radial Plots             | 43  |
| 3.2.2 Densification              | 43  |
| 3.2.3 Depth of Damage            | 44  |
| 3.2.4 Desorption                 | 45  |
| 3.2.4.1 Yield Calculation        | 45  |
| 3.2.5 Scattering                 | 46  |
| 3.2.5.1 Scattering Angle         | 46  |
| 3.2.5.2 Energy                   | 47  |
| 3.2.5.3 Vibrational Spectra      | 48  |
| 3.3 Visualisation                | 50  |
| 4 Results and Discussion         | 52  |
| 4.1 Cluster Impacts on Graphite  | 53  |
| 4.1.1 Defects                    | 53  |
| 4.1.2 Densification              | 56  |
| 4.2 Thermal Analysis             | 59  |
| 4.2.1 Effects of Energy          | 59  |
| 4.2.2 Effects of Material        | 66  |
| 4.3 Desorption                   | 68  |
| 4.3.1 Benzene                    | 68  |
| 4.3.1.1 Effects of Energy        | 69  |
| 4.3.1.2 Effects of Material      | 78  |
| 4.3.2 Effects of Projectile      | 83  |
| 4.3.2.1 C<sub>300</sub>          | 83  |
| 4.3.2.2 C<sub>840</sub>          | 89  |
| 4.3.3 Cumene                     | 92  |
| 4.4 Scattering                   | 97  |
| 4.4.1 Scattering Angle           | 97  |
| 4.4.2 Energy Distribution        | 98  |
| 4.4.2.1 Translational Energy     | 99  |
| 4.4.2.2 Rotational Energy        | 100 |
| 4.4.2.3 Vibrational Energy       | 101 |
5 Summary, Conclusions and Further Work 106

5.1 Summary and Conclusions ........................................ 106
5.2 Further Work ......................................................... 109
  5.2.1 Scattering ..................................................... 109
  5.2.2 Desorption ..................................................... 110
List of Figures

2.1 Simulation types for particle-solid interactions ......................... 20
2.2 Binary collision event sequence (courtesy of R.P. Webb) .............. 22
2.3 Binary collision approximation .................................................. 23
2.4 Impact zone in graphite ............................................................ 28
2.5 Impact points on graphite ......................................................... 28
2.6 General form of a potential energy curve - this example shows the
potential energy of a benzene molecule as a function of separation
distance from a graphite surface ....................................................... 29
3.1 Projectiles .............................................................................. 35
3.2 Flow of molecular dynamics program ....................................... 40
3.3 Benzene ................................................................................. 42
3.4 Cumene ................................................................................. 42
3.5 Benzene monolayer on graphite .................................................... 42
3.6 Cumene monolayer on graphite ------------------------------------ 42
3.7 Radial surface plot of C_60 impact on graphite. The local temper-
ature is shown as a function of distance from the impact site and
simulation time. ............................................................................. 44
3.8 Scattering angle ...................................................................... 47
3.9 Temperature analysis ............................................................... 50
3.10 Sliced target .......................................................................... 51
4.1 Penetration depth vs. molecule size ........................................... 54
4.2 Penetration depth vs. velocity .................................................... 54
4.3 Number of displaced atoms per keV as a function of molecule size
(200eV/atom, 150fs) .................................................................... 55
4.4 Number of displaced atoms per keV as a function of time (200eV/atom) 55
List of Figures

4.5 Crater formed by 10keV $C_{60}$ impact on graphite ............................................. 57
4.6 Compression of layers - in this example, due to a 500eV $C_{60}$ impact on graphite ........................................................... 57
4.7 sp$^3$/sp$^1$ ratio as a function of time after impact ........................................... 58
4.8 sp$^3$/sp$^1$ ratio at 1ps after collision of a range of molecules .............................. 58
4.9 $C_{60}$ at 4keV on graphite after 50fs ................................................................. 60
4.10 Sliced view of $C_{60}$ at 4keV on graphite after 175fs ........................................ 60
4.11 Radial surface plot of 4keV $C_{60}$ impact on graphite. The local temperature is shown as a function of distance from the impact site and simulation time. ........................................ 61
4.12 Progress of wave through target ........................................................................ 63
4.13 Example of a longitudinal wave - in this case resulting from a 250eV $C_{60}$ impact on graphite ...................................................... 63
4.14 $C_{60}$ at 4keV on graphite after 100fs ................................................................. 63
4.15 $C_{60}$ at 4keV on graphite after 150fs .................................................................. 63
4.16 $C_{60}$ at 4keV on graphite after 200fs .................................................................. 64
4.17 $C_{60}$ at 250eV on graphite after 500fs ................................................................. 64
4.18 $C_{60}$ at 1keV on graphite after 125fs ................................................................. 64
4.19 $C_{60}$ at 10keV on graphite after 125fs ................................................................. 64
4.20 $C_2H_4$ at 1keV on graphite after 125fs ............................................................... 64
4.21 $C_5H_{10}$ at 1keV on graphite after 125fs ............................................................... 64
4.22 Sliced view shows centre of target - energy is deposited into 2nd layer ............ 65
4.23 The energy of the 2nd layer is not seen in the surface ........................................ 65
4.24 Comparison of thermal behaviour following a 4keV impact on graphite and diamond ................................................................. 67
4.25 Benzene Overlayer on Graphite ......................................................................... 68
4.26 Benzene Overlayer on Diamond ....................................................................... 68
4.27 100eV impact on graphite with benzene overlayer .......................................... 70
4.28 200eV impact on graphite with benzene overlayer .......................................... 71
4.29 300eV impact on graphite with benzene overlayer .......................................... 73
4.30 500eV impact on graphite with benzene overlayer .......................................... 74
4.31 Benzene desorption yield as a function of time for graphite target at different impact energies ........................................ 75
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.32</td>
<td>Benzene desorption yield as a function of energy (after 3ps) for graphite</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>target</td>
<td></td>
</tr>
<tr>
<td>4.33</td>
<td>Fragmentation and desorption of benzene molecules due to $C_{60}$ impact</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>on graphite (after 3000fs)</td>
<td></td>
</tr>
<tr>
<td>4.34</td>
<td>Fragmentation of benzene molecules as a function of time due to $C_{60}$</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>impact on graphite</td>
<td></td>
</tr>
<tr>
<td>4.35</td>
<td>Desorption yield as a function of time for graphite target</td>
<td>79</td>
</tr>
<tr>
<td>4.36</td>
<td>Desorption yield as a function of time for diamond target</td>
<td>79</td>
</tr>
<tr>
<td>4.37</td>
<td>Comparison of 200eV impact on graphite and diamond</td>
<td>80</td>
</tr>
<tr>
<td>4.38</td>
<td>Comparison of 500eV impact on graphite and diamond</td>
<td>81</td>
</tr>
<tr>
<td>4.39</td>
<td>Comparison of 4keV impact on graphite and diamond</td>
<td>82</td>
</tr>
<tr>
<td>4.40</td>
<td>Desorption yield of $C_{300}$ impact on a graphite target with a benzene</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>overlayer for a range of energies</td>
<td></td>
</tr>
<tr>
<td>4.41</td>
<td>0.5keV $C_{300}$ impact on graphite with benzene overlayer</td>
<td>86</td>
</tr>
<tr>
<td>4.42</td>
<td>1keV $C_{300}$ impact on graphite with benzene overlayer</td>
<td>87</td>
</tr>
<tr>
<td>4.43</td>
<td>1.5keV $C_{300}$ impact on graphite with benzene overlayer</td>
<td>88</td>
</tr>
<tr>
<td>4.44</td>
<td>Desorption yields as a function of time for a range of molecules</td>
<td>89</td>
</tr>
<tr>
<td>4.45</td>
<td>2.8keV $C_{640}$ impact on graphite with benzene overlayer</td>
<td>91</td>
</tr>
<tr>
<td>4.46</td>
<td>Fragmentation and desorption of cumene molecules on graphite</td>
<td>93</td>
</tr>
<tr>
<td>4.47</td>
<td>Fragmentation and desorption of both benzene and cumene molecules on</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>graphite</td>
<td></td>
</tr>
<tr>
<td>4.48</td>
<td>300eV impact on graphite with cumene overlayer</td>
<td>94</td>
</tr>
<tr>
<td>4.49</td>
<td>500eV impact on graphite with cumene overlayer</td>
<td>95</td>
</tr>
<tr>
<td>4.50</td>
<td>1keV impact on graphite with cumene overlayer</td>
<td>96</td>
</tr>
<tr>
<td>4.51</td>
<td>Scattering angle as a function of initial kinetic energy</td>
<td>97</td>
</tr>
<tr>
<td>4.52</td>
<td>Change in potential energy per bond as a function of initial kinetic energy</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>per atom</td>
<td></td>
</tr>
<tr>
<td>4.53</td>
<td>Fraction of kinetic energy retained as a function of initial kinetic energy</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>per atom</td>
<td></td>
</tr>
<tr>
<td>4.54</td>
<td>Translational energy after impact as a function of initial kinetic energy</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>per atom</td>
<td></td>
</tr>
<tr>
<td>4.55</td>
<td>Fraction retained as translational energy as a function of initial kinetic</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>energy per atom</td>
<td></td>
</tr>
<tr>
<td>4.56</td>
<td>Fraction retained as rotational energy as a function of initial kinetic</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>energy per atom</td>
<td></td>
</tr>
</tbody>
</table>
4.57 Rotational frequency as a function of initial kinetic energy per atom 101
4.58 Fraction retained as vibrational energy as a function of initial kinetic energy per atom 102
4.59 Vibrational energy for a range of molecules after scattering from graphite 104
4.60 Vibrational frequency spectra for a C_{60} after scattering from graphite 104
4.61 Vibrational frequency spectra for C_{70} after scattering from graphite 104
4.62 Vibrational frequency spectra for C_{84} after scattering from graphite 104
4.63 Vibrational frequency spectra for a range of energies and molecules after scattering from graphite 105
Chapter 1

Introduction

1.1 Motivation

The interaction of energetic clusters with solid surfaces is of interest due to the increasing use of cluster beams in ion implantation and in ion beam analysis. This is providing an alternative to the traditional monomer ion implantation which has been used for many years. Cluster implantation has two major advantages over monomer implantation, the first of which is the ability to perform low energy implants using conventional implanters. In standard monomer ion implantation it is difficult to achieve a low energy beam using the technology currently available. Low velocity beams need a low charge density to achieve a beam of suitable length. If the charge density is high, when combined with a low velocity the charged particles separate into a central core of positively charged ions and an outer sheath of negatively charged electrons. Repulsion occurs within the core of positive ions and the beam degenerates within a very short distance. As such, either the charge density or the velocity of the particle beam is limited. As clusters only need one charge per cluster, the charge density is reduced when compared to the same dose rate with single atom beams. This enables much lower velocities (and therefore energies) to be used with cluster beams than with monomer beams. Versatility is a second advantage of cluster implantation, due to the fact that clusters have more variable parameters than monomers, e.g. the
number of constituent atoms and the species of atoms used. Preliminary work suggests that this may be a way in which to “tune” the implantation for a specific depth, and range of density and damage[1].

Secondary Ion Mass Spectrometry (SIMS) is used as an ion beam analysis technique to characterise both solids and surfaces. By sputtering material from the surface using an ion beam either a depth profile or a surface scan can be performed, depending upon the specific technique used. Recent work has shown that the use of clusters as the projectile enhances the secondary ion yield obtained [2, 3]. This is an advantage for SIMS analysis as it enables the number of projectiles needed for accurate analysis to be reduced, thus reducing the amount of damage to the surface under examination and improving the sensitivity of the technique [4].

Another area of interest is the desorption of molecules from a surface, which is of interest in work on cluster SIMS. Experimental work has shown an increased yield in intact molecules desorbed using cluster bombardment [4]. The mechanisms behind these results are examined in an attempt to understand why the yields increase and how this can be optimised. Another possible application of this work is the analysis of large molecules. The Human Genome Project is involved in mapping DNA. To do this they need to sort fragments of DNA within a sample by size in order to analyse them. Currently this is done by gel electrophoresis, which takes around four hours per sample. An alternative to this method is to use mass spectrometry, where a molecular sample is vaporised and the fragments are separated according to mass as they pass through a magnetic field. They then go to a detector for analysis and identification, the whole process taking approximately one minute. The problem with this method is that it is difficult to vaporise the relatively large gene fragments. Part of this study examines the possibility of using surface impacts of large molecules to desorb particles from the surface as a potential method of vaporising gene fragments.

The work done in this study is performed using computer simulation, a useful tool in research as it allows the examination of effects in a way not possible with traditional methods. Sensitivity tests can be performed easily, as a computer
Chapter 1. Introduction

Simulation allows just one parameter at a time to be changed. The effects of each parameter can therefore be examined in isolation. This is of great benefit when attempting to understand observed affects and their causes. Simulation and experimentation can be used together to study the assumptions and theories which are produced regarding this subject. Modelling the simulation on the suggested theoretical explanations means the theory can be verified within the controlled environment of a computer. Within the context of this work, simulations are used to investigate particle-solid interactions. Experimentally this is often done using ion beam analysis. Ion beam analysis yields information on the stoichiometry of implantation. Other analysis of materials can provide details of surface structures and mechanical, electronic and optical properties. However, for the most part, this analysis is statistical. The technology has not yet been developed to enable just one single ion to be implanted, or to follow an implanted particle at the time scales involved - of the order of picoseconds - to examine the mechanisms that lead to these observed properties. This is where computer simulation can aid the understanding of mechanisms that take place during particle-solid interactions.

1.2 Objectives

The aim of this project is to study the properties of molecule impacts on carbon based surfaces and the possible applications of such impacts, looking particularly at the use of graphite to desorb molecules from a surface. This work aims to gain further understanding of the mechanisms involved in the transfer of energy due to surface impacts and the significance of the materials involved in such mechanisms.

1.3 Novel Contributions and Achievements

A new mechanism for the desorption of surface molecules has been explored and the concept proved to be effective and comparable to current methods of desorption, while having an improved resistance to fragmentation of both molecules and
substrate. A number of papers have been published as a result of this work, as detailed below.

1. The Formation Of Diamond-like Carbon Films Due To Molecular Impacts On Graphite[5]
   Molecular Dynamics simulation is used to investigate the formation of diamond-like carbon films due to energetic impacts of large molecules such as fullerene $C_{60}$, bucky tubes $C_{100}$ and $C_{200}$ and polyethylene on a graphite surface. The local densification around the impact site and the consequent change in the bonding of both the constituent atoms of the striking molecule and the struck graphite target surface are analysed as a function of the energy per particle of the incoming molecule. Simulation data are presented in the relative probability of forming $sp^3$- and $sp^1$-bonded carbon from the energetic collision of these molecules with the surface. It is found that the ratio of $sp^3$ and $sp^1$ bonds create peaks at around 100eV per atom.

   Molecular Dynamics simulations are used to investigate the velocity distributions of a graphite lattice after being struck by carbon molecules. A temperature profile can be inferred from this velocity distribution and the “cooling” time of the ensuing thermal spike has been investigated. A range of molecule shapes and sizes for different impact energies is investigated. The kinetic energy from the impacts is seen to spread across the surface much faster than into the material in line with the properties of the thermal diffusivity of graphite. A rapid phonon transport mechanism is seen to propagate out from the impact site. The velocity of the wave is found to be independent of the molecule size, shape and energy but the amplitude and start time is dependent on all of these parameters.

   SIMS experiments using cluster ions show promising results in desorbing
intact large molecules from the surface of various materials. The optimum size, shape and energy of the clusters and the material surface has not been studied in any detail. Presented here are the results of a comparative study of gold and carbon clusters of similar total mass and energy, in particular Au$_4$ and C$_{60}$ clusters and Au$_{15}$ and C$_{100}$ clusters are compared and contrasted. The behaviour of the graphite lattice, used as the target substrate material, during the impacts is studied in detail and differences in depth of penetration, damage and energy propagation are reported.

4. Molecular Dynamics Simulation Of The Desorption Of Molecules By Energetic Fullerene Impacts On Graphite And Diamond Surfaces[8]
Molecular Dynamics computer simulations have been used to investigate the energy propagation following an energetic fullerene impact on both diamond and graphite lattices. Transverse and longitudinal waves are seen to propagate across the surface particularly for the graphite. This paper investigates the possibility of desorption of large molecules - both physisorbed and chemisorbed - from the surface due to the passage of these waves. SIMS experiments using cluster ions suggest that this could be a viable technique for desorbing large intact molecules from surfaces. So far SIMS work has concentrated on the use of metal surfaces to enhance the secondary ion emission. We investigate here the use of carbon targets - in particular graphite - where the possibility of ejection of large intact molecules is potentially greater.

5. Molecular Dynamics Simulation of the Cluster Impact Induced Molecular Desorption Process[9]
Molecular Dynamics Computer Simulation is used to investigate the effects of cluster surface interactions and their use to desorb molecules from a surface. Of interest here is the interaction of fullerenes with a graphite surface and in particular cluster impact desorption of adsorbed molecules from the graphite surface. It is shown how impacts from fullerenes on graphite cause an acoustic wave to propagate across the surface from the impact site. This wave can be used to desorb intact molecules that are
bonded by Van der Waals forces to the surface. The objective is to desorb molecules the size of genes. Using C_{60} a wave can be created which is strong enough to desorb 15 benzene molecules without breaking either the surface of the graphite or any of the benzene molecules. This will not be strong enough to desorb a high mass gene. By increasing the initial energy of the C_{60} we desorb a larger number of molecules but at the expense of breaking the surface, losing the coherence of the acoustic wave and breaking many of the benzene molecules. However, if the size of the impacting molecule is increased, to that of 300 particle "onion" type structure, it is possible to greatly increase the power of the acoustic wave. This desorbs many more benzene molecules from the surface without causing any damage to the surface, the fullerene or the benzene molecules themselves.

6. Desorption of Molecules by Cluster Impact: A Preliminary Molecular Dynamics Study[10]

A preliminary Molecular Dynamics Computer simulation has been performed to look at the use of large cluster ions in the desorption of large intact molecules from surfaces. It is found that impacts of large clusters on graphite can produce pronounced acoustic waves and that it is possible that these waves can be used to desorb large molecules from the surface. By using the acoustic wave generated by the impact of a large cluster the molecule being desorbed is gently lifted from the surface in a coordinated fashion. This is in contrast to trying to utilise the collision cascade generated by a single ion impact. In the latter case it is an infrequent event that produces a coordinated collision cascade which enables the intact ejection of a large molecule. In the former case it is the most frequent occurrence, particularly if the energy of the bombarding cluster is low. In this case also very little fragmentation of the surface or molecules occurs.


Molecular Dynamics computer simulation is used to investigate the scattering behaviour of C_{60}, C_{76} and C_{84} fullerene molecules from a graphite
surface. In particular the energy partitioning into translational, vibrational and rotational motion are determined and the vibrational frequency spectra are calculated and the principle structure identified. At the glancing angle of incidence studied here it was found that the fraction of retained kinetic energy after impact increases to about 90% as the initial impact energy increases. The fraction of energy retained as translational motion remains constant as a function of impact energy. Only a small fraction (~2%) of the energy goes into rotational motion. The rotational frequency remains constant regardless of impact energy (~5x10^{11} \text{Hz}). A number of vibrational modes can be identified easily from the vibrational spectra. In particular the C-C and C=\text{C} bonds and a “breathing” vibrational mode are seen.
Chapter 2

Background

"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" [12]

This is the working definition of a simulation given by D.E. Harrison, Jr. Although it greatly simplifies simulation, it is a starting point from which to break it into component parts:

```
Some Aspect of Nature
  leading to
  |
  v
Refine Model
  |
  v
Mathematical Model
  leading to
  |
  v
Compare Model Predictions with Nature
  |
  v
Computer Program
```
This study investigates particle-solid interactions, an area that has been researched extensively in recent years. This chapter reviews the background to the study and details current related work. The review is split into two main sections; the application of particle-solid interactions, and the mathematical modelling of the interactions and the computer techniques used.

2.1 Applications

The research currently being undertaken by the particle-solid interaction research community which is relevant to this study can be separated into four sections; particle - surface interactions, cluster projectiles, desorption and scattering of clusters.

2.1.1 Particle - Surface Interactions

Particle - solid interactions cover a wide range of applications, from ion implantation through surface modification to surface and materials analysis. Although these techniques have been around for many years, the pace of technology demands constant improvements and the development of new applications and methods as understanding of the underlying mechanisms increases. Some of these techniques are of interest within the bounds of this study and are therefore summarised below.

- Secondary Ion Mass Spectrometry (SIMS)
  Energetic primary ions bombard a surface, causing the sputtering of surface material. The secondary ions are then extracted and analysed using a mass spectrometer. There are two main methods of SIMS, the first and most well known being Dynamics SIMS. This is used for depth profiling material. The second method is Static SIMS. In this method a very low sputter rate is used such that less than a tenth of a monolayer is sputtered. In this way a surface can be scanned and analysed without significant damage.
Matrix Assisted Laser Desorption Ionisation (MALDI)

In MALDI the molecule to be analysed is combined with a matrix material that is a good absorber of a particular laser frequency. A laser is then used to vaporise the matrix, leaving the molecule intact but isolated. One of the problems with this technique is the need to select the laser frequency used so that it is only absorbed by the matrix material and not the molecule itself, which would cause fragmentation due to excessive internal energy.

The transfer of energy between projectile and surface and their associated particles is at the heart of this work - it is this which determines the behaviour of the system. As a result of the impact of a projectile on a surface, a number of reactions occur, depending upon the energy of the projectile and the materials involved. If the particles in the surface are hit with enough energy they are displaced, knocking other particles out of nearby lattice sites and creating a cascade of particle interactions. If a number of cascades develop independently which do not interact with each other, the number of defects is simply the summation of all the cascades. This is termed a linear cascade. If a large amount of energy is put into a small area of a surface, a number of individual cascades are created within a small area of the target. In this case it is likely that the cascades will overlap. Where this happens, the number of defects created and the range of damage is not simply the summation of the individual cascades. This is termed a non-linear cascade. When this gives rise to a high number of energetic particles within a small region around the impact site, it is termed a 'spike'. In his review of high density cascade effects, D.A. Thompson [13] discusses three main groups of spike models due to atomic motion:

- **Displacement Spike**

  Brinkman [14] proposed that when the mean distance between displacement collisions approaches the mean interatomic distance, there will be an outward motion of target atoms perpendicular to the path of the incident ion. This creates a crater - a central area with vacancies and a crater rim with many interstitial atoms. Evidence for this was seen by Wilson[15] using
scanning tunnelling microscopy to examine “sink holes” created on surface from ion bombardment.

- Thermal Spike
  A model was developed by Seitz and Koehler [16] for the thermal spike. At the point at which the target atoms have insufficient energy to cause collisions the remaining energy is lost as vibration to neighbouring atoms. With high energy cascade regions, the area of the vibrations overlap, causing a high proportion of atoms within a given volume to reach this state simultaneously, thus creating a thermal spike.

- Plasticity Spike (also known as shock wave)
  Where the mean velocity of the target atoms within a given volume is greater than the speed of sound within the target material, the pressure created causes compression leading to a shock wave. Such mechanisms are discussed by a number of papers, including Kitazoe[17] and Rauschenbach[18], and the quasi-shockwave model by Carter[19, 20]. Kitazoe[21] describes this as “the atoms ... play the role of a ‘hammer’ compressing the surrounding medium toward the outer direction”.

These models have been used to explain a number of effects seen in experimental studies. Ollerhead et al. reported that sputtering yields of frozen gases by MeV ions from experimental findings are not in agreement with standard sputtering theory[22]. The results are, however, consistent with the thermal spike model, pointing to a thermal spike mechanism in such materials from high energy bombardment. Marks et al. discuss the role of thermal spikes in relation to focused collision sequences, using molecular dynamics simulations of a Ni target for the study[23]. Reimann examines the contribution of pressure pulse or shock wave mechanisms to the desorption of intact large molecules[24], using the models for shock wave and pressure pulses given by Bitensky[25] and Johnson[26] respectively.

In a recent paper N.A. Marks[27] uses an analytical model to describe the cooling of a thermal spike, referred to as the liquid quench method. The system is
modelled as a hemispherical region of temperature $T_1$, with each particle of equal
temperature. The area surrounding this hemisphere is set to a temperature $T_2$
and the time taken for the energy within the hemispherical region to disperse
throughout the target is calculated.

In the example quoted[27], the thermal spike starts at time $t=0$ with a hemi­spherical region of radius $r$ set to a temperature of 5000K, with the surrounding
substrate at a temperature of 300K, where $r$ is a function of the impacting ion
energy. The heat diffusion equation

$$\nabla^2 T = \frac{c \rho}{\kappa} \frac{\partial T}{\partial t}$$

(2.1)

(where $c$ is the heat capacity, $\rho$ is the density and $\kappa$ is the specific thermal
conductivity) is used to calculate the cooling time of the spike, cooling from
5000K to 300K. This technique is limited in its usefulness for a number of reasons.
The model examines the cooling time for a thermal spike by measuring the time
taken for a drop in temperature from 5000K to 300K, with the results obtained
in agreement with both MD and quantum mechanical simulations. The cooling
time is an absolute value that is dependent upon the choice of arbitrary start
and cutoff temperatures and as such is subjective. The cooling rate is, however,
-independent of such arbitrary values and as such is a more appropriate measure
to consider. In addition, the method of modelling the hemisphere with an equal
temperature on each atom is not realistic as it ignores the fact that the centre of
the impact region would be hotter than the outer regions, with the temperature
reducing with radius.

In his recent review of MD sputtering simulations, Urbassek[28] discusses spike
phenomena with reference to sputtering. A ‘temperature’ is defined as the aver­
age kinetic energy within a given radius of each atom, converted into units of
temperature. His work shows that the ‘temperature’ of a Cu → Cu bombard­
ment 1ps after impact is considerably greater than the melting point of Cu in
some places. He also states that cluster bombardment is beginning to be studied
using molecular dynamics in order to examine the mechanisms of cluster-solid
interactions. Cluster bombardment gives high energy densities and thus gives
rise to spikes. Betz and Husinsky[29] have performed molecular dynamics simulations of a variety of sizes of Al clusters with a Cu surface for a number of energies, ranging from 0.1eV per cluster atom to 30eV per cluster atom. They show that the mean kinetic energy (maximum 'temperature') of the target atoms around the impact point depends on the energy per atom of the projectile, but that the time this temperature remains high increases with projectile cluster size. By using these two parameters the thermal effects can be 'tuned'. This is similar to the ability to control surface damage by the same parameters, energy per cluster atom and cluster size, which was shown in earlier work by Webb et al.[5] in molecular dynamics simulations of C₆₀ impacts on a graphite surface.

Webb and Harrison[30] published evidence for a hypersonic shock wave in copper, supporting Carter's shock wave model[19]. Multiple trajectories of molecular dynamics simulations of argon bombardment of copper were performed. Statistical analysis of ejected particles identified a hypersonic front moving across the surface of the copper target from the impact zone. The front is not evident in individual trajectories but can be seen when the initial positions of ejected particles are collated and examined as a function of time of ejection. These results lend support to the concept of a shock wave propagating across the target surface.

2.1.2 Cluster Projectiles

The use of cluster bombardment for applications which have previously been largely the domain of monomer implantation is increasing, although it is still a relatively small area within the particle solid group as a whole.

Molecular dynamics simulations performed by Smith and Webb[31] show the behaviour of C₆₀ impacts on graphite. A C₆₀ molecule at normal incidence reflects from the surface intact up to energies of approximately 250eV, causing depression waves and a hypersonic energy wave to move outwards from the impact site. Above 1keV the surface is broken and craters begin to form in the target. Between 450eV and 1keV the C₆₀ adheres to the surface. Smith postulates on the possibility of this as a technique for producing diamond like carbon (DLC). This
Chapter 2. Background

will be examined further in section 4.1.2.

Work by the Center for Chemical Characterization at Texas shows an enhanced secondary ion emission yield from cluster projectiles when compared to atomic projectiles [2, 3, 4, 32, 33]. The work at Texas was done using a variety of projectiles and targets including Auₙ projectiles and organic molecules with targets of gold and organic films. Blain et al. [2] performed a systematic study of secondary ion (SI) yields from a variety of targets and found an enhanced SI yield, where the enhanced yield is defined as:

\[
\frac{Y_{x_n}(E)}{nY_{x_1}(E/n)} \geq 1
\]  

(2.2)

with \( n \) the number of constituent atoms and \( Y_{x_n} \) is the yield from a projectile containing \( n \) constituent atoms. Blain gives three main points with regard to the enhanced yield:

- SI yield increases with mass
- SI yield increases with energy per atom
- SI rate of increase of yield is proportional to mass

Schweikert et al. [32] examine the use of clusters in surface modification techniques, including cluster secondary ion mass spectrometry (cluster-SIMS). Harris et al. [4] discuss the use of clusters for 'superstatic' SIMS. As a cluster has a much lower impact energy for any given velocity, it will reduce the surface damage and fragmentation caused by monatomic ions. Harris writes that the challenge for future work is to optimise the projectiles used for molecular emission, while limiting the production of ions in recombination processes [4]. He also states that the desorption process is inherently destructive by nature, which causes the fragmentation of many molecules. This results in the loss of molecular information [33]. This is where cluster SIMS may be advantageous, allowing a lower energy to be used for the same yield, thus reducing the damage created.
Chapter 2. Background

Stapel et al. [34] also found an enhancement in yield for molecular ions as compared to monomers. They also compared the results of Xe bombardment with that of SF₆, a molecular ion with similar mass. An increase in yield is seen, but no decrease in depth. This is explained by the assumption that the molecular ion fragments into its atomic components upon impact, thus creating a number of ionic impacts with much lower energy within a small region. This causes shallower cascades with an increase in energy density due to the overlapping cascades.

2.1.3 Desorption

The Department of Chemistry from Penn. State University is looking at the emission of organic molecules from overlayers on metal substrates due to ion bombardment. Garrison [35] presented results of a molecular dynamics simulation study of benzene ejection from a Ni surface using Ar bombardment. These results indicate a number of possible traits in the ejection of intact molecules, in this case benzene:

- A molecule with many internal degrees of freedom can absorb a large amount of collisional energy without fragmenting
- The ejected molecule is usually hit on at least two different points
- As the molecule is hit by an atom moving as the result of a cascade, the energy of the impact is much less than that of the bombarding ion

Taylor et al. [36, 37, 38, 39, 40] have examined the ejection processes for a number of hydrocarbon molecules from Pt due to Ar bombardment through the use of Molecular Dynamics simulations. The fragmentation patterns produced show that the majority of fragments come from single adsorbates, with only a small proportion derived from two or more adsorbates combining. It was found that a large proportion of the fragmentation to the organic molecules was caused not by direct impact from the bombarding ions, but through collision with a desorbed molecule which has been pushed across the target rather than directly removed.
perpendicular to the target. This is due in part to the mechanism used to remove molecules. By using keV impacts, cascades are created which reflect back towards the surface in some materials. These cascades hit the adsorbed molecules on the surface and knock them off. If the cascade is not moving directly upwards, some sideways motion is inevitable and it this which causes the fragmentation.

Building on this work, Žarić et al[41] then went on to use Cu cluster projectiles. This is aimed at creating multiple cascades which would increase the likelihood of a molecule being desorbed, showing an increase in the secondary emission yield of adsorbed molecules. This was done using molecular dynamics simulation of biphenyl molecules adsorbed on a Cu surface, with projectile energies ranging from 50eV per atom to 100eV per atom at an incidence angle of 45 degrees. The enhancement in yield is attributed to the increase in the number of cascades created around the impact site for clusters compared to monomers, thus providing the multiple hits per molecule necessary for desorption from the surface.

Work by Chatterjee simulating benzene monolayers on silver substrates [42] indicates that the emission of intact molecules is due to a collective motion induced by multiple hits from collision cascades. Chatterjee also discusses other mechanisms for ejection, namely the collision of a single target atom with a molecule, causing ejection. Different mechanisms leading to ejection of molecules from the overlayer are stated which can be related to the ejection angles. The first is off-normal ejection along the -30° azimuth due to collision of a first layer atom from the side of the molecule. Secondly, off-normal ejection along the +30° azimuth due to single collisions with a first layer atom below the molecule and thirdly near normal ejection due to multiple collisions.

More recently, Delcorte et al.[43] have examined the emission and fragmentation of polystyrene molecules adsorbed on silver. Delcorte[44] states that the nature of efficient collisions differ with the type of adsorbed molecule. In the case of benzene, single atom collisions cause high kinetic energy in the benzene molecule while for polystyrene the same collision causes vibrational excitation and low kinetic energy. Using simulations of Ar bombardment of polystyrene adsorbed on Ag{111}, it is shown that at initial impact energies of 5keV a large number
of high energy collision sequences are generated close to the surface. This leads to the desorption of polystyrene molecules of sizes up to 2000 daltons (a unit of mass equal to the atomic weight of a hydrogen atom). However the fragmentation patterns of the polystyrene as a result of the impact are not reported in any detail and thus are not easily compared with the work contained in this document.

Krantzman[45] shows that a range of desorbed molecules and clusters are found as a result of 300eV Xe bombardment of a benzene crystal. Both intact molecules and fragments of molecules are seen. In addition, clusters are formed as a result of the combination of fragments of two or more molecules and also as a result of the combination of fragments with crystal atoms near the surface. It is also indicated that molecules which are directly hit by the Xe projectiles fragment, while those which are desorbed as a result of collisional motion from surrounding atoms fragment due to high energy collisions but remain intact for low energy collisions.

In summary, the desorption of intact molecules by high energy atomic impacts from a range of surfaces has been shown to be due to collision sequences and correlated motion of collision sequences at the surface of the targets involved. It has been shown that although intact molecules are desorbed there is also a degree of fragmentation of the molecules involved. As the intention of this study is to develop a non-destructive method of desorption these results are not directly comparable. They do, however, give an indication of the current activities relating to the desorption of molecules from surfaces. In addition the work being undertaken in this study uses carbon targets with carbon and hydrocarbon molecules and cannot therefore be compared with the results discussed above due to the different materials involved. The overall conclusions of the work so far on cluster bombardment seem to agree that cluster projectiles produce an increase in secondary ion yield, though to what degree and the precise mechanism behind this is still a subject of much research.
2.1.4 Scattering

One method of obtaining information about the structure and dynamics of C\textsubscript{60} and related fullerenes is through the use of scattering studies, both experimental and theoretical. Classical physics states that when a beam of light hits a surface at an angle of incidence greater than that of the critical angle it is reflected from the surface at angle equal to that of the incoming angle. If this is applied to particle-solid interactions of the nature examined in this study, similar behaviour is expected. How the energy of the projectile changes, the angular distributions after impact and the possible fragmentation of the projectile all help to understand the process of particle-solid interactions further.

Busmann et al.\cite{46} performed scattering experiments using C\textsubscript{60} and C\textsubscript{70} molecules incident on graphite for a range of angles and energies. It is observed that below 200eV, no fragmentation of the projectiles occurs and the scattering angle is near specular. It is also observed that up to 95\% of initial kinetic energy is lost during the scattering process. Above approximately 450eV fragmentation is seen. It is suggested that the potential energy stored during the deformation of the projectile as it hits the surface leads to two different energy conversion mechanisms. The first is reactive, with bond breaking, which leads to slow scattering process. The second is non-reactive, with heating and acceleration of the projectile, leading to a fast scattering mechanism. This second process also has a broader velocity distribution.

The scattering of C\textsubscript{60} has been compared with single atom projectiles in the work of Hillenkamp et al.\cite{47}. Experiments were performed for C\textsubscript{60}, He and Xe projectile scattering on graphite surfaces. Earlier work\cite{48} indicated that a large proportion of scattered particles were neutral species that were too slow to be detected. For this reason, all experiments were performed at a glancing incidence angle of 75° in order to generate sufficient fast neutral molecules for statistical analysis. He scattering from graphite produces specular scattering, with a distribution consistent with a simple scattering process involving just one surface atom. Xe is a larger atom and as such is in contact with more atoms than
He. Approximately seven surface atoms are involved in the scattering process, as compared to one surface atom with the smaller He atoms. As the mass of all the atoms that the Xe atom comes into contact with is equal to the mass of the Xe atom, in effect a binary collision occurs. The scattering of $C_{60}$ is a more complex mechanism, partly due to the significantly larger number of atoms involved and partly due to the shape and nature of the $C_{60}$ itself. The distribution of the scattering angle of the $C_{60}$ molecule is narrow as in the case of the He and Xe atoms. The distribution is, however, tilted towards the surface with increasing initial projectile energy. It is hypothesised that this is due to the graphite structure. As the $C_{60}$ molecule hits the surface, kinetic energy is transferred to the surface, both parallel to and perpendicular to the surface. The layers of the graphite bend in reaction to the pressure of the $C_{60}$, shifting the effective surface position. The surface is still moving downwards when the $C_{60}$ begins to rebound and therefore there is no opportunity for the momentum gained by the surface to be transferred back to the $C_{60}$. It is this shift in position and the inelastic collision that results in a shift in scattering angle.

It appears from the research reviewed in this section that there is still a great deal to learn regarding the scattering of fullerenes. Busmann et al. reported that for energies below 200eV near specular scattering was observed with a large transfer of energy into the surface. Hillenkamp et al. state that there are different mechanisms involved in the scattering of $C_{60}$ than in the scattering of atomic particles due to inelastic energy transfer at the surface. The precise nature of the energy transfer and how this effects the scattering mechanism is still to be ascertained.

2.2 Mathematical Modelling

There are many ways to model the behaviour of materials. Which methods are chosen depends to a great extent upon what aspect of the behaviour of a material you are trying to model. In the case of particle-solid interactions there are two main choices; either by statistical methods or by theoretical models.
Chapter 2. Background

There are several different types of programs available for the simulation of particle-solid interactions, based on a variety of algorithms. They can be separated into three areas; analytical models, trajectory simulation models and quantum mechanical simulations. Figure 2.1 shows those which are currently in use. There are a number of reviews[12, 49, 50, 51, 52] on the subject of computer simulations with regard to this application area, which between them give a good general background to the principles of simulation and their practical application.

![Diagram of simulation types for particle-solid interactions](image)

Figure 2.1: Simulation types for particle-solid interactions

### 2.2.1 Analytical Models

The basis of the analytical model is kinetic theory, usually the boltzmann transport equation. This describes the behaviour of ion bombardment in terms of the depth and energy distributions of the implanted ions within the target. The equation is described in literature [52, 53] in many forms, depending upon the application it is being used for. Examples of such applications include range distributions, energy loss distributions and the calculation of channeling effects[54].

The Boltzmann transport equation is used to calculate the distribution of ions for a particular parameter such as depth or energy. It can be written in the form:

\[
\frac{\partial f(E, x)}{\partial x} = N \int [d\sigma(E' \rightarrow E)f(E', x) - d\sigma(E \rightarrow E')f(E, x)]
\]  

(2.3)
where \( N \) is the atomic density of the target, \( f(E, x) \) is the probability of finding a particle at depth \( x \) with energy \( E \) and \( d\sigma(E' \rightarrow E) \) is the probability (cross-section) of particles of energy \( E' \) having an energy \( E \) after traversing a distance \( \delta x[53] \). This equation basically calculates the probability of a particle having energy \( E \) at a depth \( x \), where the cross section is made up of particles of energy \( E + \Delta E \) that have decreased in energy to \( E \) and particles of energy \( E - \Delta E \) which have increased in energy to \( E \).

By solving this numerically, the range distribution for an ion implantation can be found. In order for this equation to be tractable a number of assumptions are made:

1. The Binary Collision approximation (section 2.2.2) applies
2. The movement of particles can be described by a number of discrete moves, each of which contains only one collision event
3. the density of particles is far greater than the number of bombarding atoms

These assumptions are valid only for a subset of implantation conditions and thus the use of this equation is limited to simple cases. However, the speed of calculation and ease of use of available programs make it a useful tool for experimental researchers to obtain quick approximations of range distributions.

### 2.2.2 Binary Collision Models

Binary Collision (BC) simulations, as the name suggests, model interactions as a series of collisions between two particles. They are also known as event-store codes, due to the way in which they work. The basic premise is that each particle is tracked as it collides with other particles. All collisions are noted and the particles involved are themselves tracked. This may be done by following the initial particle and storing data on each collision partner, returning to them in turn as the particle being tracked stops. Figure 2.2 shows the order of collisions for a typical binary collision sequence. Particle 1 collides with a particle on the
surface (collision 0). Information on particle 2 is stored and particle 1 is followed to the next collision (collision 1). This continues until particle 1 comes to a halt at collision 6. The program then returns to particle 2 and tracks it as with particle 1. This continues until all particles have come to a halt.

There are a number of variations on this, with the major differences being the order in which particles are followed. Some implementations follow the fastest particle from each interaction, some the slowest. Some implementations return to the last hit particle after the particle being traced has stopped, others go to the first particle in the list remaining. The order of calculation can be important in cases where several collisions occur within a short distance of each other. If the order is calculated incorrectly this will lead to errors in the final data. If such events occur only rarely they will not have a significant effect upon the end results, but in a dense material where such collisions occur frequently it may cause significant error.

The binary collision approximation (BCA) models a binary collision using asymptotic straight line approximations to the real path, as shown in Figure 2.3. As long as the particles are involved in no other collisions while the true and approximated paths deviate the model is valid[53]. There are situations where it
is known that the model is inaccurate, such as those which do not satisfy the above conditions. In this case the approximated paths are incorrectly calculated, leading to error.

The review of R.P. Webb [53] states three primary problems with the binary collision code:

- At low energies many-body collisions are far more likely than binary collisions.

- It cannot correctly calculate the path of a particle moving between two other particles because it must calculate the collisions sequentially as two separate interactions, leading to errors.

- BCA assumes a collision will only occur between one moving particle and one stationary particle i.e. the cascades are linear and do not overlap. In the case of high energy density cascades this is not the case. Non-linear cascades cannot be realistically modelled with BC codes due to this problem.

Binary Collision simulations usually yield statistical information with regard to the collision processes and are used extensively in scattering studies and in the calculation of sputtering yields, in addition to ion implantation range profiling.
In normal situations, many trajectories are run in order to obtain statistically significant results. This is done by using multiple impact points upon the surface, either ordered or randomly generated.

A subset of BC models is the Monte Carlo codes. These codes model amorphous targets, where the atoms within the target are randomly positioned. The probability of a collision is chosen by random numbers, thus generating random collision dynamics with the system. If the system under consideration is a multicomponent target, then random numbers are again used to determine the atom species.

### 2.2.3 Multiple Interaction Model

Multiple Interaction models, also known as Molecular Dynamics (MD) or timestep modelling, solves some of the problems with Binary Collision models. The first reported molecular dynamics simulations were in 1957 by Alder and Wainwright[55]. They modelled a 32 particle system of a face centred cubic lattice structure in order to investigate the phase transitions on a system. A later paper[56] reports results of investigations using a variety of system sizes in order to examine the effect of system size on the results of the simulations. At around the same time, Vineyard et al.[57] published work detailing molecular dynamics simulations of radiation damage in copper and later iron[58]. In all these early simulations, simple pairwise potentials were used. These papers were the first of the start of the use of molecular dynamics for a wide range of applications.

The basis of this model is the numerical solution of Newton’s laws of motion to determine the position, velocity and energy of each particle within the simulated system. Hence if a system is made up of N particles with position, velocity and acceleration \( r_i, v_i, a_i \) respectively:

\[
\dot{r}_i = v_i \\
\dot{v}_i = a_i = \frac{F_i(r_1\ldots r_n, v_1\ldots v_n, t)}{m_i}
\] (2.4) (2.5)
Where $m_i$ is the mass of the $i^{th}$ particle and $F_i$ is the force, derivable from an interatomic potential function $F_i = -\nabla V$ if $F_i$ is independent of $v_i$. This function is discussed in more detail in section 2.2.4. The very nature of MD means no assumptions are made regarding the behaviour of the collisions induced or the paths of the atoms simulated. In this way it is a very basic model, thus removing some of the problems associated with binary collision models. Molecular Dynamics methods model both linear and non-linear cascades with ease. As this method is based upon the individual particles within the system, it is able to show much greater detail than the methods mentioned so far. This means it is used for small scale research that examines single events, for example surface effects of impacts. The downside of this is that it is only possible to model systems of up to approximately half a million particles at the most using the processing facilities generally available at the current time.

### Integration Techniques

As stated earlier, molecular dynamics modelling is based upon the numerical solution of equations 2.4 and 2.5. This is done by calculating the forces on each particle at each timestep and updating the velocity and acceleration of the particle accordingly. The important parameter for optimisation of speed and accuracy in the method used is the number of force calculations required per timestep. As these calculations take a large amount of processing time it is important to minimise the number needed. There are a number of integration methods available which have been used in this area previously; a general review is given by Sanz-Serna[59] and a smaller discussion on methods pertinent to the type of work being studied here is given by Smith[52]. He suggests the use of the Verlet algorithm[60] which is known for stability and accuracy. It also involves fewer force calculations than comparable Runge-Kutta algorithms[52]. A third-order Runge-Kutta method would, according to Smith, require three force calculations per timestep as compared with just one for the method discussed below. The Verlet algorithm is based upon the following equations for position, velocity and acceleration of a particle at a given timestep $n$:
This algorithm is only second order and so small timesteps must be used in order to ensure accuracy, but has only one force calculation per timestep. A variation on this algorithm produces a third order algorithm which again has only one force calculation per timestep. The equations used for this are as follows:

\[ r_{n+1} = r_n + v_n \Delta t_n + \frac{1}{2} a_n \Delta t_n^2 \]  
\[ v_{n+1} = v_n + \frac{(a_{n+1} + a_n) \Delta t_n}{2} \]  
\[ a_{n+1} = \frac{F_{n+1}}{m} \]

The study being undertaken uses both the methods described above. The second method cannot be used alone as it requires the initial timestep values to be known and hence is not self-starting. Thus it is used in combination with the Verlet algorithm, Verlet being used in the first instance to create the initial timestep details and the third order method being used thereafter. The size of the timestep can be controlled by the program itself or set explicitly. Where a particle has large energy or velocity then the timestep is very small in order that the particle will not travel too far within one timestep. This ensures that particles do not cover a large distance between calculations, which would create error in the paths of the particles. Where the time is set within the program it is often controlled by choosing a maximum distance to travel in any one timestep and the time set according to how long it would take the fastest particle to reach that distance. The time is selected at the beginning of each timestep and checks are made throughout the integration stage. If the maximum distance is exceeded, a shorter time is selected and the integration is performed again.
Statistical Ensemble

Experimental values of many of the parameters of interest here, such as desorption yield and defect numbers, are usually the result of statistical averaging over a number of impacts. To obtain a similar number of samples with computer simulations would take years of processing time, which is not feasible. In order to obtain a similar confidence in results, however, a number of trajectories are necessary. In experimental conditions a number of parameters exist which are randomised naturally such as the impact site within a given area, the orientation of the projectile used and the angle of incidence (within given constraints). These parameters all need to be represented within any trajectory ensemble chosen for a truly representative set of results. As such the number of trajectories N needed for statistical significance increases proportional to \( N^P \) as the number of parameters P being compared increases.

For the purpose of this study two parameters are considered, those which affect the way the surface reacts to an impact; the impact site on the surface and the orientation of the molecule.

The position of impact on a target surface influences the resulting behaviour of the target. A surface atom hit directly will result in different surface and target effects that if the impact site lies between atoms. A number of impact sites should be simulated over a given region, which must be representative of the surface as a whole i.e. it must be a unit area which is repeated to make up the surface (see Figure 2.4). Care must be taken when constructing the grid that points do not lie on the boundary of the impact zone, as such points may be duplicated upon replicating the zone, with matching boundaries having twice the number of points necessary.

Regular impact sites are then set within this area. If a larger number of trajectories are needed for greater confidence in the results, this representative area can be shifted such that point A of figure 2.4 lies with in the representative area, giving a second set of trajectories which do not overlay any of those from the original set[12].
This study mainly uses $C_{60}$ as a projectile. As this molecule is spherical, the orientation of the molecule is not relevant. The other fullerene molecules are only slightly non-spherical and so any effects due to molecule orientation are minimal. These molecules are also relatively large, such that the diameter of the molecule exceeds the size of the representative area. Where this is the case, the point of impact point makes little difference to the effects of the impact[61].

The grid which has been developed for a graphite surface is shown in Figure 2.5 with 36 impact points, spaced at regular intervals.

### 2.2.4 Potentials

The modelling of forces between atoms is the most important area of molecular dynamics simulations. Such forces are described by interatomic potential functions which describe the potential energy of a system in terms of the positions of the atoms within that system.

Figure 2.6 shows the typical form of a potential energy curve. Interatomic forces generally have the same standard form, with a repulsive region for small interatomic separation distances and an attractive region for large separations. Two important parameters are the location of the potential minimum $R_{min}$ and the well depth $V$, which differ according to the atomic species involved. Potential
functions are usually developed by ab-initio data from quantum mechanical simulations or empirically by a mix of theoretical analysis to produce a basic form and parameter fitting to reproduce experimental data.

In the first case a small system is studied for which the potential function is derived through the study of the motion of atoms. This is done by first principles quantum mechanical calculations. Such a method is highly computationally expensive and as such only small systems can be studied, possibly to gain the potential functions, rather than using the method within the molecular dynamics simulation in place of the potential function. This method is beginning to be used, but is still only possible with very small systems, of the order of a few hundred atoms[62].

Empirical potentials are developed through the fitting of experimental data to a functional form that is usually derived from theoretical models. The basic form of such potentials is a pair potential, describing the potential energy between two atoms as a function of separation distance. Examples of such pair potentials include the Lennard-Jones potential [63, 64] and the Morse potential [65]. Such potentials are sufficient in the case of binary collision models where only two-body
interactions are found, but do not work well in the case of molecular dynamics where many-body interactions take place. These potentials do not take the bonding configurations of structures into account when calculating the potential energy upon a given atom, leading to errors in most materials. Such an approach works for close packed structures where the stable configuration is the point where all atoms are equally spaced and such spacing is at the potential minima in all cases. In other structures and amorphous materials, a potential is needed which takes the bonding configurations of different atoms into consideration. This suggests a form which is based upon bond angles and configurations.

Abell [66] suggests that a pair potential can be described by the general equation

\[ E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \]  \hspace{1cm} (2.12)

where

\[ V_{ij} = f_c(r_{ij})[A \exp(-\lambda_1 r_{ij}) - B \exp(-\lambda_2 r_{ij})] \]  \hspace{1cm} (2.13)

and

\[ E = \text{total energy of system} \]
\[ V_{ij} = \text{interaction energy between atoms } i \text{ and } j \]
\[ r_{ij} = \text{distance between atoms } i \text{ and } j \]

and \( A, B, \lambda_1 \) and \( \lambda_2 \) are all positive parameters.

The first term in equation 2.13 represents the repulsive part of the potential and the second the attractive part. When \( \theta = 2\lambda \) this describes the Morse potential. It is this second part which should include the bonding configuration in some way.

Abell also suggests that \( B_{ij} \) could be modelled as a function of the local coordination of an atom, dependent upon the number of bonds, the strength of the bonds and the angles between the bonds. In this case \( B_{ij} \neq B_{ji} \) due to the bonding configurations of the respective atoms. To produce a many-body potential, the
attractive component needs to incorporate a number of terms of increasing numbers of atoms. In practice however, in order to reduce the computation needed, many-body potentials are often restricted to nearest neighbour calculations, cutting the function off at a distance such that only these terms are included.

Tersoff [67, 68] developed a method based upon the earlier work by Abell which incorporates the structural chemistry of the local environment into the potential function in an attempt to overcome some of these problems. He gives $B$ of equation 2.13 as a function of the nearest neighbours of atom $i$:

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-\frac{1}{n}}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3(r_{ij} - r_{ik})^3]$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (l - \cos \theta)^2}$$

where $f_c$ is the cutoff function, $g(\theta)$ is the bond angle term and $\exp[\lambda_3^3(r_{ij} - r_{ik})^3]$ is related to bond length. The function calculates the bond strength as a function of both the angle and relative lengths of bonds for a three-body term.

Brenner [69, 70] amends Tersoff's original functional form for the case of a carbon system to correct a problem with the bond order calculations which do not model correctly conjugated bonds. This is due to a problem with the method of averaging bonds, e.g. where one atom has threefold coordination and the other has fourfold coordination. He suggests replacing the original parameter $B_{ij}$ with a modified form

$$\overline{B}_{ij} = \frac{(B_{ij} + B_{ji})}{2} + F_{ij}(N_i^{\text{tr}}, N_j^{\text{tr}}, N_{ij}^{\text{conv}});$$

where $F_{ij}(\cdots)$ is a correction term for bonding errors as a function of the number of atoms bonded to each atom and whether the bond $i-j$ is part of a conjugated system and

$$B_{ij} = [1 + \sum_{k \neq i,j} G_{ij}(\theta_{ijk}) f_{ik}(r_{ik}) e^{\alpha_{ijk}[r_{ij} - R_{ij}^{(0)} - (r_{ik} - R_{ik}^{(0)})]} + H_{ij}(N_i^{(C)}, N_j^{(C)})]^{-\delta_i}$$

(2.18)
The parameters of a functional form are usually fitted using either experimental data or ab-initio calculations or a mix of both. In the case of the Brenner potential, two parameterisations were developed in order to correctly model both hydrocarbon systems and bulk properties.

This potential function was then modified by Smith and Beardmore[71] in 1996 to further improve the bond order correction terms. The modified potential does however increase the error in the case of diamond surfaces and it is suggested the original parameterisations are used for such cases.

The Tersoff and Brenner potentials are short-ranged by using a cut-off function as mentioned earlier and thus will not accurately model the interlayer binding of graphite, which is outside of the cutoff range. It has been shown by Smith et al.[71] that this problem does not significantly effect simulations of graphite for most uses. It is however necessary to take the interlayer binding energies into account when modelling the adsorption of molecules onto a surface, or the addition of a monolayer of a second material. To this end, Smith and Beardmore[71] also developed a long-range component to the modified Brenner potential which splines a Lennard-Jones pairwise potential function[63, 64] to the short-range potential in order to incorporate the long-range forces. The form of the long-range component of this potential is

\[ V_{ij}^{ir}(r_{ij}) = F_{ij}^{cou}V_{ij}^{P}(r_{ij})f_{ij}^{lr}(r_{ij}) \]  \hspace{1cm} (2.19)

where \(F_{ij}^{cou}\) checks the short-range potential neighbour list for connectivity of atoms and \(f_{ij}^{lr}(r_{ij})\) is the long-range cut-off function. \(V_{ij}^{P}(r_{ij})\) is the Lennard-Jones 6-12 potential of the form:

\[ V_{ij}^{P}(r_{ij}) = V_{eij}[(r_{eij}/r_{ij})^{12} - 2(r_{eij}/r_{ij})^6] \]  \hspace{1cm} (2.20)

This long-range component is splined to the short-range potential such that the long-range component only comes into affect when the short-range potential component cuts off.
Chapter 3

Method

3.1 Simulation

The program used for this work was written by Keith Beardmore, who adapted it from code originally written by D.E. Harrison. This code is also currently used by several other research groups including Loughborough University (UK), University of Newcastle (Australia) and Los Alamos National Laboratory (USA). The program is a molecular dynamics simulation code written in Fortran. The analytical basis of this model is the numerical solution of Newton’s laws of motion to determine the position, velocity and energy of each particle within the simulated system. Hence if a system is made up of N particles with position, velocity and acceleration $r_i$, $v_i$ and $a_i$ respectively:

$$\dot{r}_i = v_i$$
$$\dot{v}_i = a_i = \frac{F_i(r_1 \ldots r_n, v_1 \ldots v_n, t)}{m_i}$$

Where $m_i$ is the mass of the $i^{th}$ particle and $F_i$ is the force, derivable from an interatomic potential function $F_i = -\nabla V$ if $F_i$ is independent of $v_i$. The primary potential used within this work is the Brenner potential for hydrocarbon systems[70], as discussed in section 2.2.4.
Chapter 3. Method

3.1.1 Description of Program

Initialisation

The initialisation process reads all user defined initial conditions and generates both the parameters necessary for the potential functions used and the arrays containing the atomistic data, i.e. position, velocity and energy. Many of the constants required during the simulation are also defined at this point, which including the necessary conversion factors for J → eV and Å → nm in addition to standard constants e.g. \( \pi \). The initial conditions of the simulation are the parameters which control the simulation environment. Such parameters include:

- **Projectile co-ordinates**
  For a cluster projectile they give the initial positions of each atom in the cluster

- **Projectile energy**
  The total kinetic energy of the projectile

- **Target type**
  Graphite or Diamond

- **Target dimensions**
  The maximum size used is 200Åx 200Åx 20Å, measured in Ångstroms

- **Impact site**
  The impact site is set within the target surface, given in Ångstroms

- **Integration timestep**
  This is kept constant at 0.2fs

- **Simulation time**
  Ranging from 150fs to 6ps
Projectiles

The projectiles used within this study range in size from $\text{C}_2\text{H}_2$ to $\text{C}_{840}$ and a selection of these are shown in Figure 3.1. They can be split into three groups; hydrocarbon molecules $\text{C}_n\text{H}_{2n}$; single wall fullerenes ($\text{C}_{60}$, $\text{C}_{70}$ and $\text{C}_{84}$) and “bucky onions” which are fullerene molecules consisting of two or more layers ($\text{C}_{300}$ and $\text{C}_{840}$).

The projectiles are run with a range of energies from 100eV to 12keV per molecule, depending upon the projectile and the purpose of the simulation.

![Figure 3.1: Projectiles](image)
Targets

Two substrates are used; the first is graphite and the second is diamond. The size of the target is dependent upon the type and energy of the projectile used, in order to properly contain the impact energy within the target.

In an ideal simulation the target would be of infinite size in order to avoid any edge effects which can give an incorrect picture of true events. However, due to limitations of processing power and memory, a small target area is usually simulated. The surroundings of this area are then taken into account by the use of boundary conditions. Urbassek[28] discusses four main types of boundary conditions, their use depending upon the application of the simulation.

- Free Boundaries
  With free boundaries any energy which leaves the simulated target is considered lost. This is useful for investigations such as sputtering where any particles leaving the surfaces of the target should not be returned to the target. However, it may cause problems when simulating a fluid, for example, where all atoms need to be contained within the simulation. Free boundaries are also used where there is a need to prevent wave motion from reflecting back into the lattice.

- Damping Boundaries
  In the case of damping boundaries, some energy is removed through the sides of the lattice. The amount of energy removed can be altered to suit the simulation conditions. This type of boundary is frequently used in the bottom surface and lateral edges of a target to simulate the bulk of the material.

- Fixed Boundaries
  Boundary particles can be fixed in position, giving rise to reflections from the boundaries. This can be a problem if the target is not large enough to allow for the interactions under investigation to be observed before the energy is reflected back into the target. Such boundaries are sometimes
used to prevent the target from recoiling away from an impact with a large cluster.

- Periodic Boundaries
  In the case of periodic boundaries anything leaving one side of the target re-enters on the opposite side, thus modelling a repeating lattice structure. This is often used when modelling deposition to simulate the effects of a large target.

In the simulations of this study, free boundary conditions are used with both the graphite and diamond lattices. As the area of interest is the centre of the target and is a single event, periodic boundaries are inappropriate. Both fixed and periodic boundaries would reflect any wave motion created back into the target which is not desired in this case. Damped boundaries need to be perfectly matched to the system being simulated to correctly model the bulk of a material, otherwise they do not represent a good physical model of a system.

Potential Function

As discussed in section 2.2.4, the Brenner potential is used for both the graphite and diamond, as well as the hydrocarbons used in the desorption studies. The modified parameterisation of Brenner's potential is used for the graphite and hydrocarbon molecules and the original parameters used for the diamond substrate. The initialisation stage also creates lookup tables for the parameters within the potential function.

Neighbour List

The computational speed of this program is dependent mainly upon the integration methods used and the number of atoms within the system. The integration method is chosen to minimise the number of force calculations needed as discussed earlier in section 2.2.3. According to the principle of molecular dynamics, the forces that each atom exerts upon every other atom within the system need to
be considered. For any system over a few hundred atoms this becomes extremely computationally expensive. By considering the fact that the potential has a cut-off at 5Å it can be seen that it is not necessary to consider any atoms outside the cutoff range as they will exert no influence upon the atom under consideration.

There are a number of ways to implement this concept and three of the main ones are discussed here. The simplest way of doing this is to create a spherical area around the particle which encompasses all particles which are within a specified distance. This is known as the Verlet list. The radius of the sphere is slightly greater than the cutoff distance of the interatomic potential function. The difference between these two figures is such that a particle cannot move the distance from outside the sphere to within the cutoff distance between updates of the list which is formed to include all particles which interact with the particle in question.

The second method is the ‘Method of Lights’ whereby atoms are sorted by x, y and z coordinates. Upper and lower bounds in each direction are used to select atoms within a rectangular area around the central atom for the neighbour list.

The third method, which is the one used in this study, is based on a linked list algorithm. The area of simulation is sectioned into a number of cells such that the size of each cell is no smaller in any dimension than the cutoff distance. The neighbour lists are then compiled by considering the distance only between atoms from the same cell or neighbouring cells, which is a reduction in the number of necessary comparisons. This method has obvious advantages over the Verlet list method, where all atoms need to be checked for separation distance. Comparing with the case of the method of lights, it has been shown that the linked list method is better for large simulations [52, 72].

This neighbour list is created for the first time at the initialisation stage, once the substrate has been generated. In order to minimise the extra computational time necessary for calculation of the extended potential, two neighbour lists are used; one for the short-range interactions and a second for the long-range interactions. The long-range neighbour list does not necessitate such frequent reassessment as
the short-range lists and as such reduces the time overhead taken in adding a long-range term to the potential.

Once this is completed the initial data on each atom can be calculated, using the Verlet algorithm discussed in section 2.2.3.

Main Body

Once the initialisation stage is complete the program begins the loop which constitutes the main body of the program. The program flow in normal operation is illustrated in figure 3.2. The repetition of this loop is controlled by the simulation time as set in the initial conditions.

The steps of the loop are as follows:

- If output is required for this timestep, write data.
- Check loop condition i.e. simulation time and exit loop if appropriate else increment time
- Integrate positions
- Update neighbour lists
- Calculate energies and forces
- Integrate velocities

The positions, velocities and energies of the particles are calculated according to the integration method discussed in section 2.2.3. The forces are calculated according to the potential function used.

The output from the simulation program is tailored according to the application, but the basic parameters consist of the position, velocity and energies of each atom within the system. This information is written at given times during the execution of the program, according to the initialisation parameters specified. This data can then be used in a variety of analysis programs according to application.
ASSIGN CONSTANTS
READ INITIAL CONDITIONS
READ PROJECTILE DETAILS
INITIALISE POTENTIAL FUNCTION PARAMETERS
GENERATE PROJECTILE
GENERATE LATTICE
GENERATE NEIGHBOUR LIST
CALCULATE INITIAL ENERGIES AND VELOCITIES
WRITE OUTPUT IF NEEDED
CHECK TERMINATION TIME
INCREMENT TIME
INTEGRATE POSITIONS
UPDATE NEIGHBOUR LISTS
CALCULATE ENERGY AND FORCES
INTEGRATE VELOCITIES

Figure 3.2: Flow of molecular dynamics program
3.1.2 Desorption Layers

For the desorption study an overlayer of organic material is created on the graphite. Two such overlayers are used, one containing benzene (C₆H₆) as shown in Figure 3.3 and the second containing cumene (C₉H₁₂) as shown in Figure 3.4. The overlayers are created separately and read into the program as a set of coordinates, which represent the position and atomic species of each atom. The basic method for developing an overlayer is to produce a base cell which can then be repeated to produce the required size of overlayer. The coordinates are set and the overlayer is then simulated for 1fs to stabilise the layer. The resulting coordinate set is then used for the desorption simulations. The details of each layer used is given below.

- Benzene
  The structure of a benzene monolayer on graphite has been given by both Vernov and Steele[73] and Matties and Hentschke[74] as a $\sqrt{7} \times \sqrt{7} R19^\circ$ commensurate layer, as shown in figure 3.5. This structure is in agreement with X-ray diffraction studies performed by Gameson [75]. The separation distance between the overlayer and the graphite surface is given as 3.3Å[74] to 3.57Å[73]. This agrees with our findings that the minimum energy state is at a separation distance of 3.5Å - very close to that of the graphite interlayer separation distance, 3.48Å.

- Cumene
  The structure of cumene on graphite is more difficult to find in published literature. Thus the approach for developing an overlayer is slightly different to that for benzene, in as much as the starting point consists of an overlayer of regularly spaced cumene molecules. As with the benzene layer, this layer is then simulated to find a stable configuration. This configuration is shown in figure 3.6.
3.2 Analysis

3.2.1 Energy Transfer

In order to obtain a fuller understanding of the mechanisms of energy transfer due to a projectile impact upon a substrate, the movement of energy within the system is examined through the use of thermal imaging. The simulation solves the equations of motion simultaneously for each particle and stores information on position, velocity and energy states at different timesteps. From the kinetic energies of the particles it is possible to calculate a mean square velocity of the simulated target region. From this, one could be tempted to infer a mean temperature for the region. This has been done successfully in the past for metal clusters on metal substrates[60]. In the first of these, Betz et al.[29] showed that a small region of the target arrives at thermal dynamic equilibrium within the first few 100 fs after the impact and the velocity distributions of the particles within
the region form a Maxwell-Boltzmann curve. In the second, Colla et al. [76] used a method of gliding averages to describe local temperature variations even when thermal dynamic equilibrium had not been reached for the complete region. As we are interested in the propagation of energy through the target volume we will adopt the latter scheme for this study. Previous work [6] has shown that the target does not reach a constant temperature until several picoseconds into the simulation. The energy of the impacting molecule spreads out quite quickly but there is a substantial range of temperatures in the simulated region even at quite long times. We therefore follow Colla et al. [76] and take a local volume around each particle in the simulation. The radius of the local volume was chosen to be 2.5 Å to reflect a volume containing enough particles for statistical methods while not containing so many that thermal equilibrium cannot be considered to exist. In addition, the use of a larger volume can cause small features within the substrate to be obscured by over-averaging the data. In order to visualise the local “temperature” the mean square velocity is calculated within the volume and this value is used to colour each atom during production of images (for details of image production see section 3.3).

3.2.1.1 Radial Plots

This tool produces a 2-dimensional plot of the local ‘temperature’ (see earlier) as a function of the radial distance from the impact site. This is done by averaging the local temperature around the impact site at a given radius. Viewing these plots three-dimensionally by plotting them also as a function of time allows any surface features to be followed as time progresses. Figure 3.7 shows a typical plot, in this example from a 4keV C₆₀ impact on graphite. Each timestep is differentiated by colour.

3.2.2 Densification

The densification of an area within a lattice is represented in this study by examining the coordination of atoms in the area under investigation. The local
environment of each atom is examined to estimate the coordination of the atom. If the atom has four nearest neighbours it is assumed to be in a potential sp^3 site. With three nearest neighbours, this drops to a sp^2 site. With only two nearest neighbours, sp^1 coordination is assumed. This is done very simply, without consideration of bond angles or atomic energy.

### 3.2.3 Depth of Damage

The depth of damage in a graphite lattice is approximated from the number of layers which are broken. This is done in order to produce results comparable with experimental findings. Experimentally this is done by oxygen etching of defect sites[77]. By heating samples in oxygen at 650°, holes are etched around defects sites. The hole depth extends to the deepest defect site. In this way any craters in the surface can be widened so that the depth can be probed by scanning tunnelling microscopy (STM).
3.2.4 Desorption

3.2.4.1 Yield Calculation

Experimental calculation of desorption yields using mass spectrometry are based on the measurement of molecules reaching the mass spectrometer. This depends on both the ionisation process and the energy of the desorbed molecules. In many cases the molecules fragment due to excessive internal energy before this point in time, which is approximately one second in most standard procedures. This leads to a degradation in the yield of intact molecules and increased fragment detection.

Due to the short time scales used in molecular dynamics simulations, it is impossible to reproduce the experimental method used to calculate desorption yields by simulation. As such, an alternative method of detecting fragmentation and desorption yields needs to be achieved. There are a number of issues to be addressed:

- When is a molecule considered to have left the surface?
- When is a molecule considered to remain intact?
- At what time is the yield considered?

At the point where a particle has left the surface and does not return to it, it is classed as desorbed. For the purposes of this analysis, this point occurs where the particle has moved beyond the cut-off level of the short range component of the potential. Although the long range component of the potential function is still active in this region, it is not normally sufficient to return a particle to the surface because the contribution of the van der waals forces are much smaller than the translational energy in the direction perpendicular the surface of the molecule.

The fragmentation of the desorbed particles is determined through the use of neighbour lists. A reference set of clusters from the initial positions is created containing details of the size and configuration of each cluster. This is then compared with calculated cluster configurations throughout the simulation time. All
clusters which are consistent with the reference set are classed as intact molecules. Any other clusters within the list are thus created during the lifetime of the simulation, either through fragmentation of molecules or through combination.

The problem of when to consider the yield for comparison with other impact conditions is difficult. This is due to the fact that changing parameters such as size and energy effect the timing of the desorption of surface molecules. Thus two simulation sets can differ in the time of desorption, making it difficult to compare directly in time.

### 3.2.5 Scattering

The analysis of molecular scattering can be separated into two main areas; the statistical information regarding scattering angles and energies, which can be compared to experimental measurements and the partitioning of internal energy of the scattered molecule into rotational and vibrational states. The latter cannot be directly compared to experimental findings as it is not yet possible to measure such decomposition.

#### 3.2.5.1 Scattering Angle

The scattering angle of a molecule from a surface is calculated as the deviation from the angle of approach. Thus when a molecule is scattered in a specular form, the scattering angle is given by:

\[
\theta_{tot} = (90 - \theta_{in}) + \theta_{out}
\]  

(3.1)

where \( \theta_{in} \) is the angle of approach relative to the surface normal, \( \theta_{tot} \) is the scattering angle and \( \theta_{out} \) is the angle of exit relative to the surface, as shown in Figure 3.8.

For a target coordinate system where the surface plane is \( x-z \), \( \theta_{out} \) is calculated from:
Chapter 3. Method

Figure 3.8: Scattering angle

\[ \theta_{\text{out}} = \tan^{-1} \left( \frac{V_y}{V_x} \right) \] (3.2)

where \( V_x \) and \( V_y \) are the velocities of the centre of mass of the molecule in the \( x \) and \( y \) directions respectively, the centre of mass \( (V_{x_c}, V_{y_c}, V_{z_c}) \) calculated from:

\[ V_{x_c} = \frac{1}{N} \sum_{i=1}^{N} V_{xi} \] (3.3)
\[ V_{y_c} = \frac{1}{N} \sum_{i=1}^{N} V_{yi} \] (3.4)
\[ V_{z_c} = \frac{1}{N} \sum_{i=1}^{N} V_{zi} \] (3.5)
\[ V_c = \sqrt{V_{x_c}^2 + V_{y_c}^2 + V_{z_c}^2} \] (3.6)

where \( N \) is the number of constituent atoms of the molecule and assuming all particles within the molecule are of equal mass. This is true in the case of a fullerene molecule, the case under consideration here.

3.2.5.2 Energy

The energy of a scattered molecule of \( N \) constituent atoms can be partitioned into several components:
Chapter 3. Method

- Potential energy $E_p$
  
  where
  
  $$E_p = \sum_{i=1}^{N} E_{pi} \tag{3.7}$$

- Kinetic Energy $E_k$; comprising
  
  - Translational energy $E_t$
  - Rotational energy $E_r$
  - Vibrational energy $E_v$

where

$$E_k = \sum_{i=1}^{N} E_{ki} \tag{3.8}$$

The kinetic energy of a molecule is composed of three parts, as stated above. These three components can be separated by use of kinetic theory:

$$E_t = \frac{1}{2} M V_c^2 \tag{3.9}$$
$$E_r = \frac{1}{2} mr^2 \omega^2 \tag{3.10}$$
$$E_v = E_k - (E_t + E_r) \tag{3.11}$$

$M$ is the mass of the molecule, $m$ is the mass of a particle, $r$ represents distance from the centre of mass of a molecule and $\omega$ represents angular velocity.

3.2.5.3 Vibrational Spectra

The vibrational energy of the scattered molecule contains a number of vibrational modes, including the vibration of bonds and a breathing mode. The vibrational spectra of the bonds can be calculated by examining the bond lengths over time and using Fourier transforms to obtain the spectrum of the change in bond length. Almost any periodic signal $f(t)$ can be represented as the sum of a number of sine and cosine functions, called the Fourier series. From these constituent parts the
frequency spectrum can be found. Switching between the time domain representation of a signal and the frequency domain involves two primary equations:

\[ F(\omega) = \sum_{-\infty}^{\infty} f(t)e^{-j\omega t} dt \quad (3.12) \]
\[ f(t) = \frac{1}{2\pi} \sum_{-\infty}^{\infty} F(\omega)e^{j\omega t} dt \quad (3.13) \]

where \(f(t)\) is the time domain function and \(F(\omega)\) is the frequency domain representation. Thus for a given signal \(x(t)\), the Fourier series of this function is found as \(f(t)\), then converted to \(F(\omega)\) for spectral representation. This theory is used to find the vibrational spectra of a number of variables from the scattering process:

- Bond vibration - from bond length
- Breathing mode - from fullerene diameter

This analysis is performed using the 'FFT' function in Matlab annunciator.
3.3 Visualisation

A number of programs have been developed to visualise the simulation data in a variety of ways. The main program within the group is the program 'Rayshade' which is a ray-tracing image generator, the first version of which was written by Craig Kolb, David P. Dobkin, and David C. Hoffman during 1987-1988[78]. All other programs produce output in the 'Rayshade' format for direct processing by the Rayshade program.

Temperature

Temperature uses the kinetic energies of the particles to calculate a mean square velocity of the target region, as discussed in section 3.9. Each particle is then shaded according to the mean square velocity of those particles within radius. The colour key ranges from white - indicating a "temperature" of more than 750K through to blue at 0K.

Figure 3.9: Temperature analysis
Slice Tool

In order to examine what is happening within the target during the progression of the simulation, a tool has been developed to split the target into two sections, effectively peeling away a section of the lattice to show a view of the centre of the target. This allows us to observe the effects of impacts not only on the surface of the target but also upon the bulk of the lattice, as shown in figure 3.10.

Figure 3.10: Sliced target
Chapter 4

Results and Discussion

This chapter contains the results as follows:

- Cluster Impacts on Graphite
  This section details results of simulations of cluster impacts on graphite and the effect upon the target material. The depth of craters produced by the projectile used, the amount of damage created during after impact and the densification of the material as a result of the impact are all examined.

- Thermal Analysis
  This section details the results of analysing the movement of energy around the impact site caused by the impact.

- Desorption
  This section reports the results of simulations of the desorption of organic molecules from carbon targets. Both graphite and diamond target are examined and the differences in desorption due to the two target materials is also discussed.

- Scattering
  This section includes the results of simulations of the scattering of C_{60} molecules on a graphite surface. The scattering angle of the projectile and the partitioning of the kinetic and potential energy as a result of scattering the molecule are examined as a function of the molecule size and energy.
4.1 Cluster Impacts on Graphite

Experiments have shown that where a graphite surface is bombarded with energetic projectiles, craters are formed around the impact site[77]. How the parameters of the crater, such as depth and extent of damage, relate to the projectile used is examined in this section.

Simulations of single carbon atom and fullerene impacts on graphite have been performed using a target of dimensions 100Å by 100Å by 40Å, containing approximately 50,000 atoms. Each carbon atom simulation was run for 150fs and each fullerene simulation was run for up to 2500fs. All simulations were performed using an integration timestep of $0.2\text{fs}$ and a range of energies and projectiles were simulated. The impact energies ranged from 200eV to 23keV. The projectiles used for this study are all fullerene molecules ranging in size from $C_{50}$ to $C_{200}$, with the exception of the single carbon atom projectile.

4.1.1 Defects

The depth of a crater formed by a projectile as a function of molecule size is examined. The depth is determined by the number of broken layers at the centre of the impact zone as discussed in section 2.2.3. The velocity of the projectile was kept constant throughout. Figure 4.1 shows the crater depth in the target after impact for a variety of molecules at constant velocity. It can be seen that for all the simulated molecules, the crater depth is constant. This indicates that the depth is not a function of molecule size but potentially a function of the velocity of the molecule.

A single carbon atom may not necessarily produce a crater, depending upon where it impacts upon the target surface. The distribution of penetration depth of the single atom, however, can reach the same distance as the depth of crater formed by the molecules simulated.

To investigate this further the crater depth as a function of energy is examined. Energy is a function of the mass of the projectile and the velocity, thus the crater
depth must also be a function of either mass or velocity, or a combination of both. In order to determine the relationship, the relationship between crater depth and velocity is considered. Velocity is not set explicitly within the simulation program, therefore the following identity is used:

\[ E = \frac{1}{2}mv^2 \quad (4.1) \]

Thus

\[ v = \sqrt{\frac{2E}{m}} \quad (4.2) \]

Hence \( v \) is proportional to \( \sqrt{E} \), when \( m \) is kept constant.

Figure 4.1: Penetration depth vs. molecule size

Figure 4.2: Penetration depth vs. velocity

Figure 4.2 shows a plot of the crater depth as a function of velocity for a C\(_{60}\) molecule. It confirms the relationship that penetration depth is proportional to velocity. Experimental results by Brauchle et al.\cite{77} using C\(_{60}\) impacts on graphite for a range of energies show agreement with the simulation results\cite{1}. After bombarding a graphite sample with a C\(_{60}\) beam, craters were seen to have formed on the surface of the graphite. The dimensions of these craters were measured by STM after etching the impact sites at a high temperature in an oxygen atmosphere as described in section 3.2.3. The experimental results for the depth of the craters formed are one monolayer lower than those obtained from the simulation. This difference is most likely explained by the definition
of the crater depth. In the simulations presented in figures 4.1 and 4.2, it was calculated based on the lowest broken layer. It is possible that the lowest layer may reform over a much longer period of time than the simulations are run for, hence reducing the crater depth by one monolayer.

Figure 4.3: Number of displaced atoms per keV as a function of molecule size (200eV/atom, 150fs)

Figure 4.4: Number of displaced atoms per keV as a function of time (200eV/atom)

The amount of damage produced by the impact of a projectile upon a target was examined to gain further insight into the effects caused by the impact process. For the purpose of this study a defect is classed as an atom that is not on a lattice site. Figure 4.3 shows the number of displaced atoms per keV as a function of molecule size for a range of carbon projectiles on a graphite target after 150fs. It can be seen that the number of displacements per keV is constant regardless of molecule size, except for the carbon atom. The amount of damage appears to increase linearly with energy. Thus if velocity is kept constant, larger molecules will create more damage. This is due to the fact that the total energy that is put into the surface is increased.

Closer examination of the defect pattern over time may explain why this is not the case for the single carbon atom. Figure 4.4 shows the number of defects per keV as a function of time. For fullerene molecules, the damage steadily increases over a period of 300fs. For the carbon atom, there is a peak number of defects at approximately 100fs. Thereafter the amount of damage begins to decrease. For
single atom impacts, very little damage is done and so this takes only a short period of time to stabilise. For molecular impacts, many more defects are created, however this may be due to the mechanism of calculating defects. If a layer bends rather than breaking, the atoms are still displaced from a specified atom site. This leads to the atoms in the bent layer being classed as defects. These bent layers take a much longer period of time to relax back to their original structure than is simulated here. Thus examining the displacements at a given time does not give the correct view of the amount of damage created until long after the time of impact, when all relaxation is complete and only persistent defects are then contributing to the damage range.

In summary, the depth of craters formed by fullerene impacts on graphite is a function of the velocity (and hence energy per atom) of a molecule and is independent of molecule size and shape. The number of displaced particles is dependent on the total energy of a molecule.

4.1.2 Densification

A second area of interest that may be examined from the simulation of fullerene impacts on graphite is the densification of the surface structure after impact.

It has been suggested in recent literature[79] that the use of carbon impacts on graphite as a method of creating diamond like carbon (DLC). Graphite is an sp$^2$ bonded material, while diamond is sp$^3$. DLC is a mix of both bond types, however a high sp$^3$ fraction is desirable. Examining the impact process in detail shows the mechanisms that may contribute to the densification process.

During the impact of an energetic fullerene on graphite, a crater is formed where surface layers are broken on impact. Figure 4.5 shows a side view through the centre of an impact zone, where the crater can clearly be seen. On impact, the layers of graphite are compressed, creating the right environment for the formation of sp$^3$ bonds as can be seen in figure 4.6. Depending upon the energy of the impact, these compressed layers either relax back to their original configuration or are broken by the stress created during compression. When layers break, craters are
formed, with the possibility of $sp^3$ coordination being created at the edges of the crater. Analysis gives the number of possible $sp^3$ coordinated sites at any time during a simulation. Figure 4.7 shows the level of possible $sp^3$ sites as a function of time for a 4keV $C_{60}$ impact on graphite. It can be seen that the number of possible sites increases quickly after the impact but then drops with time. This is due to the compression and relaxation of the layers. It can also be seen that the $sp^1/sp^3$ ratio drops with time. This is due to either the $sp^1$ concentration increasing, the $sp^3$ concentration decreasing, or a combination of both. It is most likely that both of these are contributing to the fall in ratio. This is attributed to the breaking of bonds in the layers as they break and form the crater, reducing the coordination from $sp^2$ to $sp^1$. The ratio of $sp^3/sp^1$ stabilises as the substrate relaxes after approximately 750fs, well within the time of the simulation.

Figure 4.5: Crater formed by 10keV $C_{60}$ impact on graphite

Figure 4.6: Compression of layers - in this example, due to a 500eV $C_{60}$ impact on graphite

Figure 4.8 shows the $sp^3/sp^1$ ratio after 1000fs for a number of different molecules over a range of energies. The size of the molecule appears to make little difference, but there is maxima for all molecules at approximately 100eV per atom. Work by Sattel et al.[79] on the formation of DLC by physical vapor deposition (PVD) using largely $C_2H_2$ species found that at energies of approximately 100eV per carbon atom, diamond crystallites are formed, which is similar to the values found here.
Chapter 4. Results and Discussion

At low energies the layers are either unbroken or only very small defects are produced with high coordination. At high energies large craters are produced with a higher proportion of opportunities for sp\(^1\) bonds to be created, given larger surface areas of the craters which are prime sites for sp\(^1\) bonding. At the maxima it would appear that the energy is sufficient to cause lasting compression, thus creating sp\(^3\) possibilities. At this energy the craters are small, leading to a minimum amount of sp\(^1\) caused by the crater edges.

The densification results indicate that although fullerene bombardment does create the conditions for substantial sp\(^3\) bonding configurations to occur, the subsequent relaxation of the target at low energies and the development of sp\(^1\) conditions at higher energies suggest however that this method needs improving in order to increase the ratio of possible bonding configurations before it becomes a viable method for DLC creation.

Figure 4.7: sp\(^3\)/sp\(^1\) ratio as a function of time after impact

Figure 4.8: sp\(^3\)/sp\(^1\) ratio at 1ps after collision of a range of molecules
4.2 Thermal Analysis

As stated earlier, the transfer of energy between projectile and surface and their associated particles is one of the major elements of this work. It is this that is examined within this section. Thermal analysis considers how energy is dissipated away from the site of impact and what mechanisms are involved. To do this, the velocities of particles are used to represent energy as this gives an indication of the direction of the flow of energy.

In this section we examine the dissipation of energy on both graphite and diamond targets due to impacts from C$_{60}$ molecules.

4.2.1 Effects of Energy

Figure 4.9 shows a typical impact of a C$_{60}$ molecule on a graphite surface. The example shown has an initial energy of 4keV at 50fs after the impact with the surface. As the C$_{60}$ is a large and spherical molecule there is little difference in the propagation of the energy for impacts at different positions on the surface or different orientations of the molecule[1]. In this figure the 'Temperature' is used to show the transfer of energy through the target as discussed in section 3.2.1. It can be seen from figure 4.9 that the impact of a C$_{60}$ creates a small crater and a central core around the crater of particles with high velocities - represented by white 'hot'. In the example shown the core reaches a maximum 'temperature' of approximately 250,000K after only 20fs. In this case the number of particles is so small that in reality it is simply a region of high velocity, fast moving atoms. However, this small area 'cools' rapidly to less than 5000K after 100fs, expanding at the same time. This represents a cooling rate of approximately 2x10$^{15}$Ks$^{-1}$, which agrees with the cooling rate obtained by Marks[27] as discussed in section 2.1.1.

As the simulation progresses, a distinct band of increased 'temperature' can be seen emanating from the impact site, transferring energy away from the central core. This is shown in figures 4.14 to 4.16. It can be seen that this band of 'hot'
particles spreads out across the surface, separating from the central core, which remains hot, gradually spreading its energy out on a longer timescale.

Figure 4.10 shows the target sliced through the centre of the impact site to give an internal view of the thermal effects. This enables the wave to be seen spreading along the surface of the target, but not down through the layers. This can be explained by the differing thermal diffusivity of graphite in plane and between the layers\[80\]; in plane, the thermal diffusivity is 30 W cm\(^{-1}\) K\(^{-1}\), perpendicular to the plane it is 0.06 W cm\(^{-1}\) K\(^{-1}\). Thus the energy is preferentially dissipated through plane.

![Figure 4.9: C\(_{60}\) at 4keV on graphite after 50fs](image1)

![Figure 4.10: Sliced view of C\(_{60}\) at 4keV on graphite after 175fs](image2)

Figures 4.17 to 4.21 show this pattern for a number of different projectiles and initial energies at different times. The wave can be seen clearly in all of them, although it is much weaker in the lower energy impacts. As the energy per atom of the projectile increases the energy is deposited further into the target. This causes the wave to spread through the sub-surface layers rather than the surface layer as seen in figure 4.22. This does not show on the surface, due to the weak inter-layer coupling of the graphite structure, as can be seen in figure 4.23.

For all energies and molecules simulated on graphite, the 'temperature' profiles have a radial appearance. Thus the mean velocities around the wave can be found and used to represent the wave with distance from the centre of the impact site. In figure 4.11 the surface 'temperature' is plotted as a function of radial
Figure 4.11: Radial surface plot of 4keV C$_{60}$ impact on graphite. The local temperature is shown as a function of distance from the impact site and simulation time.

...
acoustic wave. This can be confirmed by looking at the direction of movement of atoms relative to the impact site. Figure 4.13 shows the movement of atoms. Those that are moving away from the impact site are coloured blue, while atoms moving towards the impact site are coloured red. It can be seen that there are a number of concentric circles around the impact site, with opposing directions of movement. This is indicative of a longitudinal wave.

This is indicative of a longitudinal transfer of energy. In addition, a transverse acoustic wave can also be seen to travel across the surface for impact conditions where the surface is not excessively damaged. This can be seen in the low energy impacts, for example with an initial energy of 250eV (Figure 4.17). As the energy is increased, a large proportion of the impact energy is absorbed by the breaking of the surface and subsequent layers. This therefore prevents the increase in magnitude of the transverse wave, as an alternative sink for the impact energy is utilised.

As discussed earlier in section 2.1.3, the desorption of material from a surface has been found to be a process of the coordinated movement of the underlying material. As such, it is possible that these energy waves generated by impacts on a graphite target could be used for this purpose. The longitudinal wave dissipates energy through plane and is therefore is not suitable for this purpose, where material should be ejected from the surface perpendicular to the plane. The transverse wave, however, is ideal for this. The movement of the wave across the surface generates an upward force at the surface that could lift material from the surface of the target, thus desorbing it if sufficient energy is available. This is the subject under investigation in the next section.
Chapter 4. Results and Discussion

Figure 4.12: Progress of wave through target

Figure 4.13: Example of a longitudinal wave - in this case resulting from a 250eV C₆₀ impact on graphite

Figure 4.14: C₆₀ at 4keV on graphite after 100fs

Figure 4.15: C₆₀ at 4keV on graphite after 150fs

63
Chapter 4. Results and Discussion

Figure 4.16: $\text{C}_60$ at 4keV on graphite after 200fs

Figure 4.17: $\text{C}_60$ at 250eV on graphite after 500fs

Figure 4.18: $\text{C}_60$ at 1keV on graphite after 125fs

Figure 4.19: $\text{C}_60$ at 10keV on graphite after 125fs

Figure 4.20: $\text{C}_2\text{H}_4$ at 1keV on graphite after 125fs

Figure 4.21: $\text{C}_5\text{H}_{10}$ at 1keV on graphite after 125fs
Chapter 4. Results and Discussion

Figure 4.22: Sliced view shows centre of target - energy is deposited into 2nd layer

Figure 4.23: The energy of the 2nd layer is not seen in the surface
4.2.2 Effects of Material

The thermal behaviour of a diamond target is different to that of a graphite target. If we compare the impact of a 4keV Ce-o on both a graphite and a diamond target, several differences can be seen. Figure 4.24 shows both targets for a number of timesteps. In the initial stages both materials have the same 'thermal' appearance. On the surface of the material a circular 'hot' zone can be seen spreading outwards from the impact site (figure 4.24(a) and (b)). By 150fs noticeable differences are appearing. Whereas the graphite surface shows a distinctly separate wave breaking away from the centre area and travelling outwards, the diamond shows no such feature. At 150fs, 'hot' spots can also be seen emanating from the central area in the diamond target. If we look into the material however, it can be seen that unlike the graphite, where the wave is contained within the surface layer, the hot spots of the diamond occur through the bulk of the material (figure 4.24).

Diamond is a three-dimensional material and therefore the energy from the impact is dissipated in all directions, creating a hemispherical area of high energy around the impacts site which gradually increases in size while decreasing in energy density. Graphite is essentially a two-dimensional structure and therefore the energy is dissipated in plane in a much faster regime than through the material (across layers). As such it is unlikely that the longitudinal surface waves seen in graphite would occur in diamond, as confirmed by these results. The transverse wave which is seen in graphite, particularly at low energies, is also absent in diamond. The transverse wave is caused by the vibration of the surface layer in the case of graphite, which is a property of the material structure. In the case of diamond there is no such layered structure and therefore the conditions are not present for such a vibration to occur.
Figure 4.24: Comparison of thermal behaviour following a 4keV impact on graphite and diamond
4.3 Desorption

4.3.1 Benzene

In this section we examine the possibility of using the aforementioned transverse acoustic wave to desorb molecules from the surface of a graphite target. Of interest are the number of molecules desorbed and the fragmentation levels during this process.

The results shown here are from a number of simulations performed on either a diamond target or a graphite target of dimensions 100Å by 100Å by 20Å. In the case of graphite this contains approximately 17,000 atoms, with the diamond target containing approximately 20,500 atoms. There are 168 benzene molecules placed in the overlayer as described in section 3.1.2. This configuration is shown in figures 4.25 and 4.26. All simulations are run for 3000fs. In the case of graphite, 29 trajectories were run for statistical purposes. In the case of diamond, a single trajectory is taken as representative for qualitative results.

Figures 4.27 to 4.30 show the results of simulations performed using an energy range of 100eV to 1keV. Throughout this section, two types of image are shown; either views of the top of the target or views of the impact zone from the side, with half the target lattice cut away to show the area around the impact site.
Chapter 4. Results and Discussion

4.3.1.1 Effects of Energy

Desorption Yield

Figure 4.27 shows the impact of a 100eV $C_{60}$ on a graphite target with a benzene overlayer at progressive timesteps. As the $C_{60}$ hits the surface, the top layers are compressed. Three benzene molecules are ejected immediately after the impact as a result of ballistic motion (figure 4.27(b)). The $C_{60}$ molecule experiences compression upon impact, then relaxes back to its original spherical form as it reflects back off the surface. As the $C_{60}$ rebounds, the surface layers also expand upwards, reversing the compression of earlier stages. It is this compression-expansion process which generates a wave as discussed earlier in section 4.2. The compression can be seen at 500fs and the expansion at 1000fs in figure 4.27. This small wave is generated from the impact site and progresses through the top layer of the graphite, separating the top two layers from the third layer. As time progresses, a proportion of the energy from the impact is dissipated across the surface by the wave. It transfers energy to benzene molecules as it passes them, gradually decreasing in amplitude as it moves away from the impact point. If the energy transferred to a benzene molecule is sufficient to break both the in-layer bonding and the inter-layer Van de Waals bonding then the molecule desorbs. In the case of the 100eV impact, 9 benzene molecules are desorbed after 3000fs.

When the impact energy is increased to 200eV, the transverse acoustic wave becomes more prominent and two ejection stages can be clearly seen (figure 4.28). The first is at the point of impact, where benzene molecules are removed by the movement created from the impact and the second stage is at the point where the surface wave reaches a peak and transfers energy in an upwards motion to the benzene molecules in the overlayer causing desorption. Unlike the previous case, when the $C_{60}$ hits the surface some of the bonds break and the benzene molecule which lies under the impact site adheres to the $C_{60}$. This can be clearly seen in figures 4.28(d) to (f). At 200eV, 15 benzene molecules were desorbed after 3000fs.

If the energy of the impact increased to 300eV, a difference can be seen in the
Figure 4.27: 100eV impact on graphite with benzene overlayer
Figure 4.28: 200eV impact on graphite with benzene overlayer
substrate behaviour. Figure 4.29 shows how the graphite reacts to the impact of a 300eV C_{60} molecule. Just as in the case of the lower energy, the impact causes the ejection of benzene molecules, in this case 4 molecules (figure 4.29(b)). The impact of the C_{60} causes the compression of the top layers of the substrate as with the 100eV impact. However, in this case the C_{60} adheres to the top layer of graphite. As the C_{60} rebounds from the surface, the surface layers are prevented from reaching their full compression potential by the fact that the C_{60} is pulling in an upward direction. This forces the uppermost layers to move with it as they are attached. The top two layers separate from the substrate as before, but the acoustic wave has not been able to reach it’s maximum amplitude due to the behaviour of the C_{60} molecule, which is now bound to the surface. This action damps the surface wave by effectively pinning the impact site to the top layer of the substrate. At 300eV, 13 benzene molecules are desorbed - a decrease of 2 molecules from 200eV.

At 500eV, the C_{60} fragments and breaks the top layers of the substrate. Whereas in the case of the 100eV impact the layers compressed and then relaxed back, here the layers compress but the high energy which remains in the region of the impact site causes the breakage of bonds within the surface layers and “stitches” the top layers of the graphite substrate together as shown in figure 4.30. After 3000fs, 17 benzene molecules have been desorbed after a 500eV impact.

As the impact energy is increased further, more damage is done to the impact site and surrounding region and craters begin to form as discussed in section 4.1.1.

If we examine the desorption yield as a function of energy (figure 4.32) we see local minima in the low energy region followed by an increase for higher energies. This can be seen in figure 4.31 which shows the number of desorbed molecules as a function of time for a range of impact energies, with each set of data taken from an individual trajectory. This figure also indicates that the number of desorbed molecules increases as the energy increases. To examine this further, the desorption yield is plotted over the same range of energies, showing the number of benzene molecules desorbed after 3000fs in each case (figure 4.32). This shows an area of local maxima, followed by an increasing yield. In order to understand what
Figure 4.29: 300eV impact on graphite with benzene overlayer
Figure 4.30: 500eV impact on graphite with benzene overlayer
is happening at low energies, we must examine the images from the impact. As the energy of the impact increases, the surface wave increases in amplitude (100eV to 200eV). As the wave again increases in amplitude at 300eV, the amplitude is now such that when the wave peaks it is at the height of the benzene overlayer and they combine at the point of contact - in this case the centre of the impact. Thus the wave is damped. The increase in yield caused by the increased amplitude wave is cancelled out by the decrease caused by damping the wave. At 400eV the amplitude increases such that the yield again increases. At this point the benzene overlayer and top graphite layer once again attach, but the wave is greater in amplitude causing an increase in yield. The same increase is found at 500eV. By 700eV the amplitude is such that the top layer of the graphite actually adheres to the second layer of the graphite, causing further damping and thus the yield once again reduces.

![Figure 4.31: Benzene desorption yield as a function of time for graphite target at different impact energies](image1)

![Figure 4.32: Benzene desorption yield as a function of energy (after 3ps) for graphite target](image2)

Above 700eV, the number of desorbed molecules increases with energy. The mechanism contributing to the removal of molecules at these energies is a completely different mechanism to that seen at low energies. Figure 4.31 shows the desorption yield for a range of energies from 0.3keV to 8keV for a C_{60} impact on graphite with a benzene overlayer as a function of time. At low energies, of less than approximately 1keV, the two stages of desorption consist of an initial
ballistic removal of molecules due to the impact and a second stage related to the surface wave. At higher energies two desorption stages can also be seen. The first, as in the case of low energies, can be attributed to the ballistic removal of molecules due to the impact of a C_{60} molecule. The second stage, however, cannot be due to the acoustic wave as this no longer occurs for high energies due to the stitching of the layers. Thus another mechanism must be responsible. As craters begin to form in the surface due to the amount of energy involved in the impact and a large amount of surface damage is created. It is suggested that the benzene molecules in the overlayer are ballistically removed by collisions cascades from the damaged substrate, as suggested by Garrison et al. (see section 2.1.3). As the amount of damage increases, the number of molecules desorbed also increases.

**Fragmentation**

The second area of interest in studying the desorption of materials is the level of fragmentation caused. Figure 4.33 shows the number of benzene molecules which fragment during the simulation period over a range of energies for a C_{60} impact on graphite, with the desorption yield for comparison. For low energies very little or no fragmentation is seen; both the target surface and the overlayer remain intact. As the energy increases, the target sustains damage due to the impact. As discussed in section 4.1.1, as the energy of an impact on graphite increases, craters begin to form on the surface. This behaviour is also seen on graphite with an overlayer of benzene. As the damage to the graphite increases, so the number of fragmented benzene molecules also increases. If the time at which fragmentation occurs is examined (figure 4.34), it can be seen that for the higher energy impacts, most of the fragmentation occurs within a relatively short period of time after impact.
Chapter 4. Results and Discussion

Figure 4.33: Fragmentation and desorption of benzene molecules due to C₆₀ impact on graphite (after 3000fs)

Optimisation

As stated earlier, the aim of this study is to examine the possibility of the use of surface acoustic waves in graphite to desorb large biomolecules intact for mass spectrometry. In the ideal case, a high desorption yield is needed, combined with no fragmentation of surface damage. If the results so far are examined, it is possible to find an optimum energy at which these needs are best met. Figure 4.33 shows both the desorption yield and the fragmentation numbers for the range of energies studied. The fragmentation of the benzene molecules occurs at energies above approximately 500eV. This is also a local maxima in the desorption yield and thus it is suggested that this is the optimum desorption energy in order that no damage is caused to the surface or the molecules under examination. The next step is to improve the desorption yields. Results show that if the impact energy is increased, the number of molecules that are fragmented increases significantly, due to the layers ‘stitching’ together and damping the acoustic wave from propagating. In order to increase the yield without increasing the fragmentation, the amplitude of the acoustic wave needs to be increased without causing damping. One way of doing this is to increase the size of the cluster projectile used and this will be discussed in section 4.3.2.
4.3.1.2 Effects of Material

As discussed earlier, when a C\textsubscript{60} hits a graphite target at low energies it causes the desorption of a few benzene molecules and generates a surface wave. When a low energy C\textsubscript{60} hits a diamond target, however, the behaviour is different. Figures 4.37 to 4.39 show both graphite and diamond targets for comparison.

Figure 4.37 shows the impact of a C\textsubscript{60} molecule at 200eV on both a graphite target with benzene overlayer and a diamond target with benzene overlayer. A range of timesteps are shown. With the graphite target, the C\textsubscript{60} hits the target and compresses the substrate as discussed earlier. Two benzene molecules can be seen to desorb from the overlayer in figure 4.37 in contrast to the diamond target, where no desorption can be seen to occur. After the impact, the C\textsubscript{60} reflects from the graphite surface (figure 4.37(e)), whereas the C\textsubscript{60} remains on the diamond surface between the substrate and the overlayer and forms bonds with both (figure 4.37(f)). Although the surface wave can be seen in the case of the graphite it can not be seen with the diamond target.

At 500eV the impact causes ejection of benzene molecules from the diamond target as well as the graphite. The impact causes the stitching of layers with the graphite surface. On the diamond surface the layers are compressed by the impact of the C\textsubscript{60} molecule which loses shape and adheres to the surface as a cluster of carbon atoms. At this energy on the diamond target one or more of the benzene molecules are broken by the impact. A hydrogen atom can be seen in figure 4.38(d) above the surface which indicates that one of the benzene molecules has fragmented causing ejection of a hydrogen atom. At a time of 1000fs, two intact benzene molecules can be seen above the target in figure 4.38(f). After a time of 2000fs, 15 benzene molecules have been desorbed from the graphite target, compared with 3 benzene molecules from the diamond target.

Figure 4.39 shows the simulated particles for timesteps 0fs, 500fs and 1000fs as with the other energies discussed. When the impact energy reaches 4keV there is little difference between the graphite and diamond targets in terms of the substrate behaviour after the impact of a C\textsubscript{60} molecule. Both targets are
significantly damaged as can be seen in figure 4.39. In both cases, a crater is formed around the impact site and mixing of layers can be seen. Benzene molecules are ejected ballistically due to the cascades created by the impact.

Figure 4.35 shows the desorption yield with time for graphite while figure 4.36 shows the same set of data for diamond. While the graphite data shows two distinct stages in the desorption process, no such distinction can be seen in the diamond data. The desorption from the diamond target appears to happen soon after impact, in much the same way as the fragmentation of molecules occurs in the graphite case. This indicates that the desorption of the molecules in the case of diamond is instigated by ballistic movement due to the impact as opposed to surface wave behaviour as seen in the graphite. This is in agreement with the findings in section 4.2.2, where no surface wave is seen to occur in diamond substrates.

![Figure 4.35: Desorption yield as a function of time for graphite target](image1)

![Figure 4.36: Desorption yield as a function of time for diamond target](image2)
Chapter 4. Results and Discussion

Figure 4.37: Comparison of 200eV impact on graphite and diamond
Figure 4.38: Comparison of 500eV impact on graphite and diamond
Chapter 4. Results and Discussion

Figure 4.39: Comparison of 4keV impact on graphite and diamond
4.3.2 Effects of Projectile

It has been shown that in order to increase the desorption yield, more energy is needed at the surface. However, it was also shown that too much energy can cause stitching together of layers. Thus, a method is needed of increasing the size of the transverse wave without causing the layers to stitch together. This section examines the effects of using larger clusters as projectiles, looking at the change in desorption and fragmentation as a function of size. Two large clusters are used; C_{300}, a two layered fullerene cage and C_{440}, a three layered fullerene cage.

4.3.2.1 C_{300}

Figure 4.41 shows the impact of a C_{300} molecule with 0.5keV impact energy on a graphite target with an overlayer of benzene. It can be seen in figure 4.41(c) that during the impact, the benzene molecule which is sited directly on the impact site is trapped underneath the C_{300} molecule. On hitting the surface, the C_{300} compresses, also compressing the layers beneath the impact site due to the large downwards momentum. By 1500fs the C_{300} is beginning to rebound from the surface as can be seen in figure 4.41(d), leaving the surface intact. Benzene molecules are desorbing from the surface, which is attributed to the impact itself. The trapped benzene molecule is also beginning to move away from underneath the C_{300} molecule. Figure 4.41(e) shows the C_{300} molecule has escaped the surface intact by 2000fs. The surface wave is also beginning as can be seen by the separation of the top two layers from the rest of the substrate. At 2500fs (figure 4.41(f)) the top two layers are moving back towards the target, showing the surface wave still occurring. A large number of benzene molecules can also be seen to have desorbed by this time. 15 benzene molecules have desorbed from the overlayer after 3000fs, with no fragmentation. The C_{300} escapes from the surface intact.

If the impact energy is increased to 1keV, differences can be seen in figure 4.42 of the behaviour of the graphite target as a result of the C_{300} impact. As in the
case of the 0.5keV impact, the C\textsubscript{300} hits the surface and compresses. Desorbed benzene molecules can be seen in figure 4.42(c) as a result of the impact. The surface layers of the graphite also compress, and the benzene situated on the impact site is trapped beneath the C\textsubscript{300}. As the C\textsubscript{300} rebounds the trapped benzene once again moves away. However, as the C\textsubscript{300} attempts to escape the surface it collides with and becomes bound to a benzene molecule, which can be seen in figure 4.42(e). The benzene molecule then prevents the C\textsubscript{300} from leaving the surface and it instead turns the C\textsubscript{300} back towards the surface (figures 4.42(e) and (f)). This, in turn, damps the surface acoustic wave originally created by the impact. It does not however damage the surface, which remains intact. After 3000fs, 51 benzene molecules have desorbed from the overlayer. The C\textsubscript{300} eventually comes to rest on the surface of the graphite target, with no damage to the surface itself. The benzene sited on the impact point is fragmented, but all other benzene molecules are intact.

Figure 4.43 shows the results when the impact energy is increased to 1.5keV. The impact causes the top three layers to vibrate. However, it can be seen in figure 4.43(c) that the impact damages the surface, stitching together the top two layers. The momentum of the C\textsubscript{300}, however, pulls the surface upwards with it, causing wave like movement of the central area around the impact site. This leads to the desorption of a large number of benzene molecules. After 3000fs, 75 benzene molecules have been desorbed. The surface is damaged as a result of the impact. Two benzene molecules are fragmented.

The desorption yields for each of these simulations are plotted in figure 4.40. It can be seen that the desorption yield increases with the impact energy. The results from C\textsubscript{60} impacts on the same target type showed two stages of desorption as described in section 4.3.1.1. Figure 4.40 appears to show the first stage of the desorption process, with the large increase in yield leading to the second stage being clearly visible in the cases of the 1keV and 1.5keV impacts. One reason for the slower development of the desorption process could be that the surface wave may take longer in the case of a larger projectile. This could generate a slower vibrational frequency of the surface, leading to longer timescales.
Figure 4.40: Desorption yield of $C_{300}$ impact on a graphite target with a benzene overlayer for a range of energies

It is suggested that the energies studied here are in an equivalent region of the desorption curve to the low energy $C_{60}$ impacts. The 1.5keV $C_{300}$ impact causes the stitching of layers which indicates that fragmentation will begin to occur upon an increase in energy.
Figure 4.41: 0.5keV $C_{300}$ impact on graphite with benzene overlayer
Figure 4.42: 1keV $C_{300}$ impact on graphite with benzene overlayer
Figure 4.43: 1.5keV C$_{300}$ impact on graphite with benzene overlayer
Here we examine the desorption of overlayer molecules by means of $\text{C}_8\text{40}$ impacts. The target sizes are increased in order to properly contain the effects of the impact. Figure 4.45 shows the impact of a 2.8keV $\text{C}_8\text{40}$ molecule on a graphite target with a benzene overlayer. It can be seen in figure 4.45(b) that the $\text{C}_8\text{40}$ molecule compresses the surface upon impact, behaving in much the same way as the $\text{C}_3\text{00}$ molecule discussed in the previous section. Whereas the $\text{C}_3\text{00}$ molecule trapped a single benzene underneath it, more than one benzene molecule can be seen to be trapped underneath the $\text{C}_8\text{40}$. This is expected, as the diameter of the $\text{C}_8\text{40}$ molecule is approximately three times that of the $\text{C}_3\text{00}$. Figure 4.45 at a time of 1000fs shows single hydrogen atoms indicating fragmentation of benzene molecules has occurred. A few benzene molecules can be seen in the initial stages of desorption. By 1000fs, it can also be seen that the $\text{C}_8\text{40}$ molecule is attached to the surface in a number of places. It can be seen that the surface wave begins by 2000fs, with the top four layers splitting away from the remainder of the substrate.

![Figure 4.44](image)

Figure 4.44: Desorption yields as a function of time for a range of molecules

By 3000fs 38 benzene molecules have been desorbed. This is lower than the number of benzene molecules desorbed by the $\text{C}_3\text{00}$ molecule, which is not what would
be expected. The desorption yield for the 2.8keV C\textsubscript{840} is not correctly calculated due to the analysis method used. The analysis counts a benzene molecule as being desorbed if it is more than 2Å above the surface. However, this does not take into account movement of the surface itself, which pushes the benzene molecules in the overlayer above the cutoff distance without being desorbed. This occurs in the case of the C\textsubscript{840} molecule due to the large wave it generates. As the surface moves up and down, peaks and troughs occur in the desorption yields that are an artifact of the analysis method rather than an effect of the impact. This is not the case for the 4.2keV C\textsubscript{840} impact, which has a smaller wave due to damping. Here the desorption yield is calculated correctly to be 38 benzene molecules at 3000fs and 113 benzene molecules at 5500fs. Once again the yield at 3000fs is lower than that of the C\textsubscript{300} molecule at comparable velocity. If we examine the desorption yields as a function of time it can be seen why this occurs. Figure 4.44 shows the desorption yields as a function of time. It can be seen that the second stage of the desorption process begins at 2300fs for a 1.5keV C\textsubscript{300} impact. However, it does not begin until 3000fs in the case of the C\textsubscript{840}. This is attributed to the fact that in the case of C\textsubscript{840} four layers are involved in the surface wave, whereas in the case of the C\textsubscript{300} molecule only two layers are involved. The extra layers mean that the surface vibrations set up which cause the surface waves will have a lower frequency due to an effectively higher mass. More work needs to be done to develop a method of effectively comparing different projectile desorption yields as simply comparing at a specific time has been shown to be an inaccurate representation of events.
Figure 4.45: 2.8keV $C_{840}$ impact on graphite with benzene overlayer
4.3.3 Cumene

To determine if this method of desorbing molecules would also work for larger molecules, simulations have been run with cumene overlayers on graphite. These simulations use the same target size as the simulations run with a benzene overlayer; 100Å by 100Å by 20Å. The configuration of the cumene overlayer used is discussed in section 4.3.3. C\textsubscript{60} was used as the projectile, with a range of impact energies from 300eV to 8keV. All simulations were run for a period of 3000fs with an integration timestep of 0.2fs.

Figures 4.48 to 4.50 show the impact of a C\textsubscript{60} molecule on a graphite target with cumene overlayer for energies of 300eV, 500eV and 1keV respectively.

Figure 4.48 shows that a 300eV C\textsubscript{60} impact on the cumene overlayer causes the fragmentation of at least one cumene molecule. Figures 4.48(c) to (f) show hydrogen atoms and fragments of a cumene molecule. Further investigation has shown that the molecule which fragmented is initially situated directly on the impact point. As with the benzene overlayer, the graphite layers bend due to the impact of the C\textsubscript{60} and a surface wave is generated. This can be seen in figure 4.48(c), where the top two layers of the graphite surface are lifted up at the start of the wave. These two layers appear to be stitched together. After 3000fs, 3 cumene molecules have been desorbed, in comparison with the benzene overlayer which generated 13 desorbed benzene molecules.

Figure 4.49 shows a 500eV C\textsubscript{60} impact on a cumene overlayer. As with the 300eV impact, fragmentation of a cumene molecule is evident by the hydrogen atoms seen in figure 4.49(b) and (c). The top layers can be seen stitched together in figure 4.49(b) to (f). 9 cumene molecules are desorbed after 3000fs, in comparison with the benzene overlayer which generated 16 desorbed benzene molecules.

Figure 4.50 shows a 1keV C\textsubscript{60} impact on a cumene overlayer. The intact desorption of at least two cumene molecules can be seen. It can be seen that the first four layers of the graphite are joined around the point of impact by the damage created during the impact. Just as in the 700eV impact on a benzene overlayer, this has the effect on reducing the desorption yield. For an impact of 1keV on a
cumene overlayer, 12 cumene molecules are desorbed during a period of 3000fs. For the same energy on a benzene overlayer, 17 benzene molecules are desorbed.

The number of cumene molecules desorbed and the number of fragmented cumene molecules are shown in figure 4.46 as a function of energy. The molecule which is sited at the point of impact is almost always broken during impact as it is struck by the incoming projectile, but otherwise the cumene molecules seem remarkably averse to fragmentation, with the number of breakages similar to those for the case of benzene. The number of molecules desorbed appears lower than benzene, indicating that it is slightly harder to desorb the cumene molecules from the surface than to desorb benzene molecules. This may be due to the increase in the potential for internal energy in the cumene molecules due to the increased number of bonds. The yield is however still significant for the low energies used. The structure of minima and maxima at low energies seen in the benzene desorption yield can also be seen for the cumene molecule desorption yield. It does, however, appear to be shifted slightly, with minima at 300eV and 700eV in the case of benzene desorption yield and at 1keV and 2keV in the case of cumene desorption yield. It is suggested that this occurs due to the increased energy that is taken up internally in the overlayer, thus increasing the amount of impact energy needed to stitch the layers together.

![Figure 4.46: Fragmentation and desorption of cumene molecules on graphite](image)

![Figure 4.47: Fragmentation and desorption of both benzene and cumene molecules on graphite](image)
Figure 4.48: 300eV impact on graphite with cumene overlayer
Figure 4.49: 500eV impact on graphite with cumene overlayer
Figure 4.50: 1keV impact on graphite with cumene overlayer
4.4 Scattering

Computer simulations are used to investigate the scattering behaviour of fullerene molecules from a graphite surface. The scattering angle and energies are examined as a function of molecule size and energy. The partition of energy into translational, vibrational and rotational components are determined and vibrational frequency spectra are calculated.

4.4.1 Scattering Angle

![Scattering angle graph]

Figure 4.51: Scattering angle as a function of initial kinetic energy

Figure 4.51 shows the mean scattering angle for a range of energies from 500eV to 2.8keV for three fullerenes; C\textsubscript{60}, C\textsubscript{76} and C\textsubscript{84} at an angle of incidence of 80°. The error bars represent one standard deviation, which is approximately 2.5% for all measurements. At low initial energies, the scattering angle is close to the specular scattering angle. As the energy increases, the scattering angle deviates more from the specular scattering angle. The C\textsubscript{60} scattering angle results are in agreement with the scattering angle found by the work done by Hillenkamp et al.[47] for C\textsubscript{60} impacts on graphite as discussed in section 2.1.4. Hillenkamp suggests that C\textsubscript{60} scatters in a non-specular fashion from graphite due to surface behaviour.
It can be seen that there is a greater deviation from the specular scattering angle with the C\textsubscript{76} than with the C\textsubscript{60}. It can also be seen however, that the scattering angle of the C\textsubscript{84} falls between the C\textsubscript{60} scattering angle and the C\textsubscript{76} scattering angle. This could indicate that the shape of the molecule being scattered is a factor in determining the scattering angle, as the C\textsubscript{76} is not as spherical as either the C\textsubscript{60} or the C\textsubscript{84}.

In summary, the scattering angles of the fullerene molecules examined are dependent upon the size and shape, as well as the initial energy of the molecule.

4.4.2 Energy Distribution

The change in potential energy per atom as a function of the initial energy per atom for C\textsubscript{60}, C\textsubscript{76} and C\textsubscript{84} is shown in figure 4.52. The change in potential energy increases as a function of energy for all molecules investigated. This is likely to be due to the increased deformation of a molecule as the scattering energy increases. Increased deformation leads to an increase in the strain upon the bonds of a molecule, thus increasing the potential energy. As the potential energy increases more, bond breaking occurs due to excessive strain. It can be seen that the change in potential energy of the C\textsubscript{76} molecule increases more than the C\textsubscript{60} or
Chapter 4. Results and Discussion

C₈₄ molecules. This is in agreement with the findings of the study of vibrational energy (to be discussed in section 4.4.2.3) which show greater fragmentation of the C₇₆ with increasing energy than the other molecules.

Figure 4.53 shows the percentage of the initial kinetic energy that is retained after the scattering event. Data is shown for C₆₀, C₇₆ and C₈₄ with an energy range of 500eV to 2.8keV. The percentage of energy retained changes only slightly with the value of initial kinetic energy. At approximately 8eV per atom, 83% of the initial energy is retained. When the initial energy is increased to approximately 30eV per atom, the amount of energy retained has increased by only 7% to 90%. The data in figure 4.53 indicates it is possible that this value saturates at approximately 90%. The percentage of energy retained is similar for each fullerene, indicating that the size and shape of the molecule is not a factor in the retention of energy during and after the scattering event.

The retained kinetic energy is partitioned into three components; translational, rotational and vibrational energy.

4.4.2.1 Translational Energy

Figure 4.54 shows translational energy as a function of the initial energy per atom for the three fullerene molecules under investigation. It can be seen that all the fullerene molecules retain the same energy in translational movement for a constant initial energy per atom. This indicates no size or shape effects are present in the value of translational energy.

Figure 4.55 shows the fraction of the retained energy which is taken up in translational energy. For all molecules the translational energy fraction of the retained energy is constant for all energies investigated. For a C₆₀ molecule, 97% of the retained kinetic energy is taken up in translational energy. For a C₇₆ molecule, the value falls to approximately 76%. A C₈₄ molecule uses 69% of the retained energy in translation. The fraction of energy used in translation appears to decrease with increasing molecule size. This is expected as all molecules have the same translational energy regardless of size or shape. As molecule size increases,
the total energy of a molecule increases for a constant energy per atom. Thus, as the total energy increases with molecule size, the amount of energy that is partitioned into translational energy stays the same. Therefore, the fraction of the total energy which is translational decreases.

In summary, it is found that the amount of energy taken up in translational movement is independent of the shape or size of the molecule. The fraction of retained kinetic energy taken up in translational movement is independent of the initial kinetic energy, but is related to the size of the molecule.

![Figure 4.54: Translational energy after impact as a function of initial kinetic energy per atom](image)

![Figure 4.55: Fraction retained as translational energy as a function of initial kinetic energy per atom](image)

4.4.2.2 Rotational Energy

Figure 4.56 shows the fraction of retained energy taken up in rotational energy. The rotational frequencies are shown in figure 4.57. The rotational frequencies of the fullerene molecules appear to be constant for all energies investigated. The C\textsubscript{60} molecule rotates at a frequency of approximately $3.6 \times 10^{11}$ Hz. The C\textsubscript{76} has a rotational frequency of approximately $4.4 \times 10^{11}$ Hz and the C\textsubscript{84} rotates at a frequency of approximately $2.9 \times 10^{11}$ Hz. While the C\textsubscript{84} molecule has a lower frequency than the C\textsubscript{60} molecule, the frequency of the C\textsubscript{76} molecule is higher than that of the C\textsubscript{60}. It can be inferred from this that the shape has some effect upon
Chapter 4. Results and Discussion

the rotational frequency. It can also be seen that the size of the molecule is of relevance to the frequency of rotation.

The rotational energy is calculated from the rotational frequency of the molecule as discussed in section 3.2.5. It can be seen in figure 4.56 that very little of the retained energy goes into rotational motion - under 2%. As the initial energy per atom increases the fraction of retained energy taken up in rotational energy decreases. At low energies a difference can be seen in the fraction used by each molecule. As the energy increases, these differences get smaller, appearing to converge at approximately 35 eV per atom.

In summary, the rotational frequency of a scattered molecule is dependent upon both the size and shape of the molecule. The energy of the molecule does not appear to be significant.

![Figure 4.56: Fraction retained as rotational energy as a function of initial kinetic energy per atom](image1)

![Figure 4.57: Rotational frequency as a function of initial kinetic energy per atom](image2)

**4.4.2.3 Vibrational Energy**

The kinetic energy which is not accounted for in either translational or rotational motion is classed as vibrational energy. Figure 4.59 shows the fraction of energy used in vibrational motion as a function of the initial energy per atom. It can be seen that the fraction of energy used in vibrational energy is constant with energy.
per atom. The amount of energy taken in vibrational motion therefore increases with the size of the molecule. For a $C_{60}$ molecule it averages 2%, increasing to 23% for a $C_{76}$ molecule. 30% of the retained energy goes into vibrational motion for a $C_{84}$.

![Graph showing the fraction retained as vibrational energy as a function of initial kinetic energy per atom.](image)

Figure 4.58: Fraction retained as vibrational energy as a function of initial kinetic energy per atom

There are two main aspects of the vibration of a fullerene molecule; bond vibration and molecular vibration. The increase in vibrational energy with size can be explained by considering the components of vibrational energy. A proportion of the vibrational energy goes into 'breathing mode' vibrations, which is the vibration of the whole molecule. The remainder is used in bond vibrations. As the molecule increases in size, there is an increase in the number of bonds within the molecule. These extra bonds take up extra energy in vibration, hence increasing the overall vibrational energy.

Figures 4.60 to 4.61 shows the vibrational spectra for $C_{60}$, $C_{76}$ and $C_{84}$ for energies from 500eV to 2.8keV. These spectra were obtained by Fourier analysis as discussed in section 3.2.5.3. Figure 4.63 shows the same spectra plotted to compare each molecule for the same initial energy per atom.

Figure 4.60 shows the spectra for the vibrational modes of a scattered $C_{60}$ af-

102
ter impact. Three principal modes can be seen at $3 \times 10^{12}$ Hz, $4.5 \times 10^{12}$ Hz and $1.5 \times 10^{12}$ Hz. The first two modes correspond to the vibrational frequencies of C-C and C=C bonding. The third mode is attributed to a 'breathing mode'. This is the pulsing of the whole molecule where the diameter of the molecule increases and decreases periodically. This can also be seen by performing Fourier analysis of the mean diameter of the molecule, which gives a value in agreement with the above frequency.

As the energy increases the background levels increase. There is also an increase in the spectral density at low frequencies ($\leq 1 \times 10^{13}$ Hz). When the spectra for C$_{76}$ are compared with those of C$_{60}$, the same principal modes are seen in both, however the C$_{76}$ shows more background noise than the C$_{60}$. Significant differences are seen in the low frequency range of the C$_{76}$ - a far higher spectral density is seen than for the C$_{60}$ molecule for a wider spectrum. In this case high levels are seen for frequencies less than $2 \times 10^{13}$ Hz, particularly at the higher energies shown. The low frequencies are an artifact of the measurement technique and can be attributed to bond-breaking. When a bond breaks, any bond vibration is lost and the bonds usually simply move further apart. Where analysis is restricted to bonds which are within 2 bond lengths, the low frequency components are much reduced. However, these low frequency components give a good indication of the level of bond breakage within the molecule. This can be seen clearly on the C$_{76}$ spectra, where the low frequency component increases significantly above $1.9$ keV, where bond breakage begins to occur.

The vibrational frequency spectra of a C$_{84}$ molecule after scattering are seen in figure 4.62. Once again the three principal modes can be seen as in the case of the C$_{60}$ and C$_{76}$. The range of the high density frequencies is approximately the same as that to the C$_{60}$ molecule, smaller than for the case of the C$_{76}$, indicating a higher level of bond breaking than the C$_{60}$ but lower than the C$_{76}$.

To summarise, it is found that the main vibrational frequencies of the fullerene molecules examined after a scattering event can be attributed to C-C and C=C bonding, with a third frequency relating to a 'breathing mode'.
Figure 4.59: Vibrational energy for a range of molecules after scattering from graphite

Figure 4.60: Vibrational frequency spectra for a $C_{60}$ after scattering from graphite

Figure 4.61: Vibrational frequency spectra for $C_{76}$ after scattering from graphite

Figure 4.62: Vibrational frequency spectra for $C_{84}$ after scattering from graphite
Figure 4.63: Vibrational frequency spectra for a range of energies and molecules after scattering from graphite
Chapter 5

Summary, Conclusions and Further Work

5.1 Summary and Conclusions

The simulation of fullerene interactions with graphite and diamond surfaces has led to a greater understanding of the behaviour of both the graphite and diamond materials and the fullerene molecules studied during and after molecule-surface interactions.

The response of a graphite target to the impact of a fullerene molecule was examined and the observed features were explained. When a fullerene molecule hits a graphite surface at energies over 1keV at normal incidence, craters are formed at the impact site. Features of these craters have been examined and can be associated with parameters of the impact such as energy and velocity. The depth of a crater has been found to be a function of the velocity of a molecule only. The size and shape of a molecule has not been found to relate to the depth of the crater formed. The number of displaced atoms around the impact site has been found to increase as the total energy that a projectile puts into the target as a result of an impact is increased. This total energy is again not affected by the size or shape of the molecule involved. These results can be used to 'tune' the crater sizes according to the projectile type. The number of displaced atoms is
controlled by the total impact energy, while the depth of the crater is controlled by the energy per atom. Thus by changing the number of constituent atoms but maintaining the same total energy, different depths of crater with the same amount of surrounding defects can be created.

Another aspect of this work was the examination of the use of fullerene impacts to change the density of the target material. It has been shown that the craters and surrounding damage caused by the impacts contain a high proportion of potential sp\(^3\) bonding sites. However, these sites are mostly attributed to the compression of layers within the graphite target. Such compression tends to relax over a period of time back to its original configuration and therefore the increase in potential sp\(^3\) bonding sites is seemingly transient. This method, of fullerene bombardment, therefore does not seem to have the potential for creating a high sp\(^3\) fraction using the impact parameters examined here, but subsequent investigation may develop the concept further.

For lower energy impacts (≤2keV) the surface behaves in a completely different way. Up to energies of approximately 450eV the surface remains unbroken as a result of the impact of a C\(_6\) molecule at normal incidence. Thus the energy transferred to the surface needs to be transported away from the impact point in a manner other than by ballistic collisions. This energy transfer is carried out by surface waves, both transverse and longitudinal. The longitudinal wave is much faster than the transverse wave, but carries less energy. In both cases, the speed of the waves are independent of the initial energy of the projectile. These waves are not however seen in diamond, suggesting that they are an artifact of the layered structure of graphite.

The transverse wave caused by projectile impact lends itself to use for desorbing molecules from a graphite surface due to the coordinated upward movement of the surface atoms of the target. A number of fullerene molecules have been shown to successfully desorb molecules from both benzene and cumene overlayers. Benzene molecules are desorbed from an overlayer placed above a graphite substrate with impacts of fullerene molecules with energies as low as 100eV. If the energy of the projectile is increased too much the layers of the graphite substrate are stitched.
together, causing damping of the wave due to the inability of layers to vibrate freely. As the energy increases further, damage is created at the impact site and some molecules within the overlayer are fragmented. At these higher energies, the desorption yields also increase and this is attributable to both thermal desorption and ballistic collisions from high energy cascades at the surface of the graphite. Thus, there appears to be an optimum initial energy whereby the fragmentation is low but the desorption yields are high. This occurs before the layers begin to stitch together. The desorption yield has also been shown to increase with increasing molecule size. However, this is not seen when using a diamond target, where overlayer molecules are removed purely as a result of surface cascades as there is no transverse wave present. Thus the concept of using graphite substrates to desorb molecules by means of surface waves appears to be proven.

At very low energies and or low angle of incidence fullerene molecules are scattered intact from a graphite surface. It has been shown in this study that the scattering angle of a fullerene molecule is dependent upon the size and shape, as well as the initial energy of the molecule. The partitioning of energy after a scattering event was also examined. It was found that the percentage of the initial impact energy that is retained by a molecule is a function of the initial projectile energy. It is however independent of the size or shape of that molecule. This energy is split into three types of energy: translational, rotational and vibrational energy. It is found that the amount of energy taken up in translational movement is a function of energy. It is independent of the shape or size of the molecule. A large proportion of the retained energy goes into translational energy; for the molecules studied the fraction ranges from 76% to 97% depending upon the size of the molecule. The fraction of energy that goes into rotational energy is small in comparison, under 2% in all cases. The rotational frequency of a scattered molecule is dependent upon both the size and shape of the molecule but the energy of the molecule does not appear to be significant. The main vibrational frequencies of the fullerene molecules are the same for all molecules and are found to be consistent with the C-C and C≡C bond vibrational frequencies at 3x10^{12} Hz and 4.5x10^{12} Hz. A third vibrational mode is found to be that of a ‘breathing mode’ at 1.5x10^{12} Hz. Hence
it is shown that the majority of the retained energy goes into translational and vibrational energy which are a function of the initial energy and not the size or shape of the molecule being scattered. Only a small part of the retained energy, that of the rotational energy, is dependent upon the size and shape of the molecule being scattered.

In conclusion, it has been shown that the defects produced by fullerene impacts on graphite surfaces are to a large extent 'tunable' by the nature and energy of the fullerene molecule used. It has been shown that the use of large cluster impacts to desorb molecules from graphite substrates is an effective mechanism which causes little or no damage to either substrate or molecules. This provides an opportunity for multiple impacts for higher desorption yields without sample degeneration due to fragmentation. It has also been shown that the scattering of fullerene molecules from graphite surfaces is only slightly dependent upon the shape and size of a molecule and the primary parameter in such scattering events is the impact energy for a constant angle of incidence.

5.2 Further Work

There are a number of areas within this study that would benefit from further research. These can be split into two main areas; scattering and desorption.

5.2.1 Scattering

- Orientation of Molecules
  The orientation of molecules with respect to the surface is not examined within the bounds of this work. Although it is of little importance for spherical molecules such as C_{60}, other fullerenes such as C_{76} may behave differently when scattered at different orientations, in much the same way as a rugby ball bounces depending upon how it lands.

- Vibrational modes
  The vibrational modes of fullerene molecules need to be examined in much
greater detail. Such information may give greater insight into the structure and characterisation of molecules such as CeO, which are relatively new molecules in scientific terms.

5.2.2 Desorption

It has not yet been possible to compare the results of this study on desorption with experimental findings due to a lack of experimental research in this area. One of the most urgent aspects of future work is therefore the development of a programme to study this desorption method experimentally in order to confirm the feasibility of this approach to desorption.

The constraints of time has meant that examining the long term desorption yields has not been possible and so direct comparison of desorption yields has not been done. Future work could involve developing analysis tools to correctly compare desorption yields obtained from simulations of different time scales.

This study uses relatively small molecules in the proof of the concept of impact induced desorption. Realistically, much larger molecules such as long-chain polymers need to be simulated to find an upper limit on the size of molecules that can be desorbed using this technique. Larger projectiles also need to be examined to find an optimum size for projectiles used in the desorption of molecules from surfaces. Changing the atomic species of the projectiles may change the reaction of the surface. Changing the target material to other layered structures should produce similar effects to graphite. If the interlayer bonding is of a different strength and the interlayer separation is different, then the optimum impact energies should change, along with the energy at which the layers stitch together.

It may be possible to set up a standing wave on a surface using multiple impacts at the same point. This would be interesting to simulate, but the timescales involved would be exceptionally long in terms of molecular dynamics code. As such a method of simulating both short and long term effects efficiently needs to be developed.
Bibliography


[44] A. Delcorte and B.J. Garrison. Desorption of large organic molecules induced by kev projectiles. *Accepted for publication in Nuclear Instruments &
Bibliography


