Computer simulation of nanoindentation into carbon materials

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Computer simulation of nanoindentation into carbon materials

by

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An M.Phil thesis
Submitted in partial fulfilment of the requirements for the award of

Master of Philosophy

of

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Abstract

A molecular dynamics simulation is set up to analyse the nanoindentation process on graphite and diamond. A model for the indenter and its movement is developed. Different potential descriptions for graphite are tested as well as different surfaces for diamond. Results are analysed in terms of force-distance curves and lattice distortion. A comparison with experimental results is also made. The use of parallel programming has also been examined.
Acknowledgments

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Contents

1 Introduction 1

1 Methodology 4

2 The Simulation technique 5

2.1 Basic set up of the MD code 5

2.2 Parallel programming 7

3 Modelling of the system 13

3.1 Geometry and movement of the diamond tip and the interface 13

3.2 Interaction model for tip crystal contact 16

3.3 The structure of the graphite crystal 17

3.4 The structure of the diamond crystal 18

3.5 The interaction model for the carbon system 19
II Results and Conclusion

4 Simulation results

4.1 Results for graphite with the Nordlund potential

4.1.1 Small crystal

4.1.2 Big crystal

4.2 Results for the graphite with van der Waals potential

4.2.1 Small crystal

4.2.2 Big crystal

4.3 Results for the diamond

4.3.1 \{010\} surface

4.3.2 \{111\} surface

4.4 Discontinuities and the interlayer term

4.5 Planar forces

4.6 Energetic results

4.7 Reconstruction

5 Experimental results

5.1 The shape of the indentation

5.2 Calculating mechanical properties

5.3 Experimental force-distance curves
5.4 Comparison .............................................. 78

6 Conclusion, Criticism ..................................... 80
  6.1 Conclusion ............................................. 80
    6.1.1 Graphite ........................................ 81
    6.1.2 Diamond ......................................... 82
    6.1.3 General .......................................... 82
  6.2 Criticism ............................................. 83

III Appendix ................................................. 84
  A Damping ................................................. 85
  B Potentials .............................................. 87
    B.1 The ZBL potential and its parameters ............. 87
    B.2 The Tersoff potential and its parameters .......... 88
    B.3 The Nordlund extension and its parameters ......... 89
    B.4 The cut-off function for the Lennard-Jones potential . . . . 89
  C Movie .................................................... 91

IV References ............................................. 94
Chapter 1

Introduction

A standard way to obtain mechanical properties of a solid body is to observe how the material reacts towards indentation. A tip is pressed into the bulk and both deformation of the bulk and the force experienced by the tip are characteristics for the mechanical behaviour of the bulk and the tip. If a tip of standard material is used such investigations determine mainly the behaviour of the solid body.

With the development of nanotechnology the investigation of mechanical properties on a nanoscale becomes more and more important. It may be necessary to examine material behaviour on local spots rather than looking at the average behaviour of large surfaces. The properties of thin films are especially interesting. These are particularly difficult to observe and interpret because of their small dimensions and also the influence of the substrate is likely.

To apply investigations of mechanical properties to nanoscale materials, a new technology called nanoindentation is used. In this a nanosize tip is forced into the solid body on a small scale. The characterisation of the indentation is given by the maximum penetration depth and by the repulsive force experienced by the tip as a function of the indentation depth. Normally this is also accompanied by scanning force microscopy (SFM) so that an image of the indentation region...
is also provided. The shape of the force-depth curve represents in some way the mechanical properties of the tip and the solid body over the range of the interaction depth. With the use of very small forces this range is very small and it is therefore possible to investigate mechanical properties of thin films or nanoscale materials. The normal choice for the tip material is diamond because it is the hardest material available.

The method has recently developed into commercial use. However, despite the nanoscale size of the measurements, the techniques cannot yet provide atomic scale information during the indentation. Information about atom exchange between tip and bulk or development of bonded structures is not available. To overcome this gap the use of computer simulation seems a promising way forward, since it allows investigations on smaller forces and distance scales than can yet be examined in experiments.

The Vickers indentation method has been used and studied over the years and different variations of the application have been realised [SO93]. A particular interesting point is the influence of the shape of the tip [FS95]. The elastic-plastic contact problem behind the obtained force distance data was already considered over 100 years ago by Hertz [Her82]. The analysing process has been developed and improved on over the years. [OP92].

In recent years the idea of nanoindentation has been introduced to apply this technique to the nanoscale. An attempt to investigate coating structures can be found by Li et al. [LCC+94]. Tsui et al. [TOP96] examined how the results for mechanical properties depend on the applied stress. They discovered similar effects to conventional indentation. Concentrating on carbon materials, Umemura et al. [UAHM96] improved the understanding of amorphous carbon. They were able to show the order of hardness between different carbon materials. Carbon has attracted special interest because of nuclear applications. Kanari et al. looked at these systems [KTBE97] and obtained elastic-plastic and fully plastic results. Examinations are not limited to carbon systems and
investigations in pure metal systems have also been conducted [BCB98]. The SFM technique [RTFG92] is also an integral part of the nanoindentation process. A review of the combination of the two can be found by Baker [Bak97].

Computer simulations have been of increasing importance in recent years and various methods have been developed and applied in many different fields [WP99]. One of the different methods developed over the years is 'Molecular Dynamic Simulation' [Hee86, AT87] further referred to as MD. Its basic approach consists of calculating forces for each atom involved in the interaction and then applying dynamics according to Newton’s laws of motion. Therefore, it has become a powerful tool for studying atomic motions and interactions [Urb97]. Its main advantage is the good description of dynamic behaviour on the atomistic scale, while its main drawback is the extensive use of computing time. Few computer simulations of nanoindentation have been carried out so far. Harrison et al. conducted many simulations on diamond [HBWC91, HWCB92, HWCB95] in which they investigated indentation whereby they observed adhesion between tip and bulk as well as fracture and atom transfer. A completely different approach can be found by Bolshakov et al. [BOP96]. They used finite elements to examine aluminum. Glosli et al. showed results not only for indenting, but also for sliding on the surface of amorphous carbon [GPB95]. Basic work has also been done by Pätzold et al. [PLHH97] who looked at polymer films using molecular dynamics. Kompououlos et al. put the effect of repeated indentation at their centre of interest [KY97].

It is the aim of this work to develop a program which allows the systematic simulation of nanoindentation experiments with carbon materials. A model for the tip and its movement is developed as well as conditions for the use on graphite and diamond. Corresponding experimental work is also carried out and an attempt to combine the two approaches is also made.
Part I

Methology
Chapter 2

The Simulation technique

In this chapter the structure of the code used for the simulations is shown. Boundary conditions and basic settings are explained. Some basic steps and problems with the use of parallel programming are explained.

2.1 Basic set up of the MD code

Simulations are carried out using an MD code of standard form. Thereby the crystals are represented through structureless points. Between these points forces are calculated obtained from classical potentials. The dynamic processes are then described by numerically integrating the classical laws of motion. In the present work integration is achieved through a Verlet-algorithm [AT87]. The timestep is fixed to 1 fs.

For simplicity of the calculations, units inside the programme are defined in an appropriate way which are all approximately $O(1)$ during the calculations. The basic units used are Å, eV, and carbon mass for length, energy and mass respectively. This gives the force a dependent unit eV/Å (corresponding to approximately 1.6 nN). This unit is used in all force diagrams obtained by simulation.
CHAPTER 2. THE SIMULATION TECHNIQUE

To speed up the simulations, the interactions are not calculated between all atoms but only between those which are in a reasonable distance of each other. For further improvement there are neighbour lists created for each atom which contain all particles inside the interaction radius plus all particles which are outside this but inside a so-called skin radius. Therefore the list has not to be updated every step but only when particles move the distance of the skin radius \[AT87\]. Therefore in every step the distance moved by the fastest particle is calculated. All these distances are added together and if this sum reaches 80 percent of the skin radius the lists are updated. This rather generous limit creates safety even in the worst case assumptions. However the case studied in the present work only includes small motions and does not extend to these worst cases.

In reality the size of the crystal can be treated as infinite compared to the scale of the indentation. So in a real structure there is no influence from the boundary of the crystal.

However, limited computer power and therefore simulation time forces the computer model to deal with an unrealistically small crystal compared to the scale of the experimental indentation. Boundary effects may occur. It is therefore necessary to introduce boundary conditions which give the small crystal the behaviour of an infinite crystal. In the present work a rectangular crystal is used where the surface is free and all other sides experience a damping proportional to the velocity of the atoms. With the graphite this damping includes the 4 outermost atoms of every plane and also the bottom layer. For diamond it is the 2 outermost elementary cells in every direction. The model behind these conditions is to simulate the natural thermal conductivity see also appendix A. In addition to that the two outermost atoms on each layer of the graphite and the outermost elementary cell on the side of the diamond are fixed. These atoms can therefore not move in space. This condition prevents the crystal from moving away in space and is necessary to give stability. It corresponds to the real world in a way that the crystal is fixed to an experimental device or is part of a larger slab of material.
CHAPTER 2. THE SIMULATION TECHNIQUE

2.2 Parallel programming

As mentioned earlier, simulations are restricted in size and length due to limited computing power. One way to deal with this situation is the use of parallel computers. In these the calculations are divided among several processors and carried out at the same time. The idea is best explained using loops. Consider the following FORTRAN loop.

\[ a = 10 \]
\[ \text{do } i=1,10000 \]
\[ b(i) = i \]
\[ \text{enddo} \]
\[ \text{do } i=1,10000 \]
\[ b(i) = b(i) + a \]
\[ \text{enddo} \]

Looking at the second loop one processor takes \( i \) and calculates \( b(i)=b(i)+a \) for \( i \) reaching from 1 to 10,000. Having 2 processors available, one can calculate the numbers from 1 to 5000 and the other can calculate the numbers from 5001 to 10000 at the same time. Obviously this requires special computing facilities and programming techniques, which shall be explained here to some extent.

There are various approaches to parallel programming. Most of them requiring a special coding for the system right from the start of the programming work. The way in which it has been investigated in this work, is to use the existing FORTRAN sequential code and add parallel commands according to the OpenMP standard. This is about to become a standard and has the advantage to use existing codes and parallelise them later in a second step.

In this procedure the first step is to optimise the sequential code. To do so, there exists a variety of programming tools. For example in FORTRAN 'tocf'
and 'prof' which tells how much time parts of the programme cost. This may lead to changes in the structure of the calculations (rearranging the algorithm). It may also suggest technical changes such as avoiding real numbers or power functions. Of course this depends on the compiler and libraries. Therefore a general description for this can not be given.

Given a working optimised sequential version in the second step OpenMP commands are used to tell the compiler which loops are to be dealt with in parallel. The following text will present a simple example to show basic concepts. As a rule, an OpenMP command must start in the first column of a line. For detailed command information, specifications and exceptions, the reference manual is to be consulted. Reference can be found in the OpenMP manual [Ope97] and to some extent in computer based manuals like those for 'pfa', 'auto-par' and others.

Given the FORTRAN loop from above a parallel version may look something like in the next example.

```fortran
a = 10
do i=1, 10000
    b(i) = i
enddo
do i=1, 10000
 !$OMP PARALLEL DO
 !$& default(none), private(i), shared(b,a)
    b(i) = b(i) + a
enddo
```

Line 6 in this example tells the compiler that the next loop will be parallel. Several processors will work on it at the same time, each dealing with a particular range of values. In the 7th line there are some declarations to define the status of variables in the parallel region. For all variables in a parallel region such a declaration has to be made. The 'default' can set the preferences or as here...
show there are none. The two important commands are ‘private’ and ‘shared’. The first one has the effect that a local copy of the specified variable is given to every processor. These are no longer associated with the physical memory of the originally defined variable. Therefore, all local copies are undefined by entering the parallel region and by leaving it the original variable is undefined. ‘Shared’ declares a variable to be shared among all processors. They all see one copy associated to one (the original) memory place. Therefore an initially given value to this variable is seen by all processors. If several processors try to change the variable it is undefined at the end of the parallel region. Because all have accessed the same memory place and no assurance can be made which change is valid.

From the previous discussion, it is clear that one has to be very careful about the way in which variables are used and data is changed. The main problem which has to be considered is called data dependency. This means that different processors want to read or write to the same physical memory position. If this happens the results get undefined and therefore, unpredictable. The following simple example will give more detail.

\begin{verbatim}
a = 10
do i=1, 10000
   b(i) = i
endo

do i=1, 10000 !$OMP PARALLEL DO !$& default(none), private(i), shared(b,a)
   b(i) = b(i) + a + b(i+1)
endo
\end{verbatim}

In line 8 a processor may be dealing with a current value of \( i \). It then needs the value of \( b(i) \) and also the value of \( b(i+1) \). But it could be that the later
value is just in use with another processor. If now both of them try to access this particular memory at the same time the value may become undefined. There are some OpenMP standard commands to deal with such a situation. These are the 'atomic' command for a single line and the 'critical' command to enclose several lines. The idea is that these commands tell the compiler that inside a parallel region certain commands are dangerous and are not allowed to be processed by different processors at the same time. However, to behave accordingly the processors have to communicate with each other at each of these areas to make sure they wait for each other. This slows down the simulation time so that all the time saved by parallelising could be lost in these waiting time slots. The next piece of FORTRAN code gives an example for use of the 'atomic' command.

```
a = 10
do i=1, 10000
  b(i) = i
enddo

!$ OMP PARALLEL DO
!$& default(none), private(i), shared(b,a)
b(i) = b(i) + a
!$ OMP ATOMIC
  b(i) = b(i) + a + b(i+1)
enddo
```

Another important feature is the 'reduction' clause. Consider the loop to be as follows.

```
a = 10
do i=1, 10000
  b(i) = i
```

In this case each processor gets a private copy of c. At the end of the parallel region all values for c from all processors are combined in the way the sign in the reduction clause states it (in this case they are added together). This final value is then assigned to the original memory place of c. The major problem with this is that reduction clauses do not operate on arrays. Also, if the reduction happens in a subroutine inside the parallel region the reduction clause only works if the variable is passed as an actual parameter.

Another important clause is 'schedule'. By the use of this it is possible to tell the compiler in which way it should divide the task between the different processors. This is explained given the example from above and assuming two processors (A,B). One way to divide the task would be i=1 to 5000 for processor A and i=5001 to 10,000 for processor B. Also it could be the first 10 to A and the next 10 to B the next 10 to A and so on. There are many different possibilities and it is impossible to give any recommendation about the best, because it completely depends on the specific calculation task. The only approach is to try different ways and test the time use of the calculation until the best result is found.

In the present work the attempt was to calculate the force between one atom and all its neighbours in parallel. This choice was made because this loop is responsible for 90% of the calculation time. The two main problems were the multi-body kind of the interactions and the dynamics of the system. The first automatically develops data dependencies because a particle which is first
neighbour for one atom may be second neighbour for another. If both atoms are calculated at the same time the location of this neighbouring atom must be known in both tasks. The second is due to changes in the neighbourhood because of atomistic movement. Atoms which used to be neighbours of one particle are now neighbours of another particle, the corresponding memory has to be transferred from one processor to the other. A working parallel version could only be obtained by use of 'atomic' and 'critical' sections around all readings of location values and around all writing of force values. Thereby the parallel program was slowed down so that it finally became slower than the single processor calculation. The attempt to rewrite the program completely to allow parallelisation was not pursued because of the time limit of the project. Also a result was that the program could have been parallelised more efficiently if the reduction clause would work on arrays. If this were to be made possible the OpenMP standard would allow a parallelisation of the present program to be completed successfully.

From the points raised above it is clear that with a parallel program one has to be very careful what the single parts of the program are doing and how they interact. There are also many rules for use of the OpenMP commands which are to be studied carefully. Testing and time comparison becomes a fundamental task during parallelisation. Results have to be compared to single processor calculations to make sure there are no hidden data dependencies left. Time cost has to be tested for different parallel versions to see if there is an advantage in doing it. The result of all this may also be that a program in its present structure can not be parallelised by just using OpenMP commands but has to be rewritten to obtain algorithms suitable for further parallelisation.
Chapter 3

Modelling of the system

The computing model to describe the diamond tip is explained, together with the basic geometry of the tip. Also the models used for the graphite and the diamond are given. Furthermore the model of the interactions inside the crystal and between crystal and tip are explained.

3.1 Geometry and movement of the diamond tip and the interface

To simulate the diamond tip the following approach is used. An interface which has the geometry of the tip used in experiments moves towards the surface in a sinusoidal way. The atomic structure of the tip is ignored. Nevertheless the model contains most of the necessary experimental features.

The geometry of the tip is shown in 3.1. The line \( CH \) marks the direction of movement. Simulations are only carried out where this line is perpendicular to the surface. Therefore, the plane \( ABD \) lies parallel to the surface. In experiments this plane corresponds to a \( \{111\} \) plane in the diamond tip. While in experiments there is an aberration from the ideal pyramid, the simulated
tip has perfect rectangular planes intercepting at $C$. To show the relation to a diamond tip it is also marked where the \{001\} plane lies. If the interface is indented to a depth $h$ the triangular cross section $ABD$ has an edge length of $a = \sqrt{6}h$ and therefore, an area of $A_c = \frac{3}{2}\sqrt{3}h^2$. The total contact area consists of 3 triangles $ABC$, $ACD$ and $BCD$. The total area is $A_t = 4.5h^2$. Figure 3.2 gives the way $A_c$ and $A_t$ vary as a function of $h$.

Figure 3.2: Total and triangle cross section of the interface.

To bring this geometry into a model, the interface is set up by defining 4 vectors for the 4 vertices of the pyramid. All other structural values can be obtained.
from these vectors. Simulations are restricted to a vertical impact without any angle distortion. Hence, during the movement of the interface only the z-coordinates of the vertices change. Again all changes in the structural values can be obtained from the altered vertices vectors.

It is important to choose the start point of the tip at a height such that the surface is out of the range of the ZBL potential. The ZBL potential is defined in 3.2. Also the height of the interface itself must be large enough, otherwise the interaction would include an empty area above the interface. This could lead to discontinuities in the calculation and should therefore be avoided.

The movement of the interface is defined by calculating the time dependent z coordinate according to

$$z(t) = z_{\text{start}} - (A + z_{\text{start}}) \sin\left(\frac{\pi}{T}t\right)$$ \hspace{1cm} (3.1)

where $z_{\text{start}}$ is the initial z position of the interface tip, $A$ is the maximum penetration depth, $T$ is the total simulation time for a full indentation and retreat of the interface and $t$ is the time elapsed.

This way of modelling sets a fixed indentation depth and moves the interface in a sinusodial way over the distance. In reality a force is applied to the tip and it moves as far as possible. But since force and depth are correlated it makes no real difference which of the two is the given parameter. The only drawback is that the interface cannot adjust its velocity to reactions from the crystal (see comment on results in section 4.1). From this model the given time for the complete simulation also determines the velocity of the interface in the following way

$$v_{\text{interface}} = - (A + z_{\text{start}}) \frac{\pi}{T} \cos\left(\frac{\pi}{T}t\right)$$ \hspace{1cm} (3.2)

with $v_{\text{interface}}$ as the velocity and the other parameters as mentioned above.

The velocities which are thereby produced in the simulations (averaged speeds of the movement are defined by $2(A + z_{\text{start}})/T$ and lie between $32ms^{-1}$ and $380ms^{-1}$) are several magnitudes higher than in experiment (typically $v_{\text{interface}} = 2 \times 10^{-5}ms^{-1}$). This has to be considered while discussing the results.
3.2 Interaction model for tip crystal contact

The interaction is modelled in a pure repulsive way according to a carbon-carbon ZBL potential. The ZBL potential [ZBL85] only depends on the distance $r$ between the interacting atoms. The analytical form is

$$V_{ZBL}(r) = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 r} \sum_{i=1}^{4} c_i e^{-\frac{a_i r}{2}}$$ (3.3)

with atom numbers $Z_1$ and $Z_2$ as the only material dependent constants. $Z_1$ representing carbon is equal to 6, while $Z_2$ representing the interface is a priori undefined. It seems as a sensible choice also to set it equal to 6 which makes it a carbon-carbon ZBL potential. For all other parameters see appendix B.1.

At the cut-off radius the potential has to be cut smoothly. Therefore, the following cut-off function

$$f_{c}(r) = \begin{cases} 
1 & : r < R \\
\frac{1}{2} + \frac{1}{2} \cos(\pi \frac{r-R}{S-R}) & : R < r < S \\
0 & : r > S 
\end{cases}$$ (3.4)

is multiplied to the ZBL potential. $R$ is chosen equal to 2.5 Å and $S$ equal to 4.0 Å, after tests have shown these to be reasonable choices.

The ZBL potential only depends on the distance between two interacting particles. Hence, for every atom the perpendicular distance to the interface must be calculated. To do so the interface is divided into seven parts, the tip vertex, the 3 faces facing the crystal and the 3 edges between them. For each atom it is checked if it is perpendicular to one of these parts. If so, the distance is calculated. After all seven parts have been checked the smallest of the calculated distances is taken. For this one it is then tested if it is inside the range of the ZBL potential and the force is calculated if so.
3.3 The structure of the graphite crystal

In graphite the carbon exists in $sp^2$ hybridisation. This leads to a layer structure of hexagons with a strong binding in the layers and a weak binding between the layers. In general graphite is highly anisotropic in these two major directions. The basic cell (hexagonal) is shown in figure 3.3 where also the layer structure is clear to see. The nearest neighbour distance is 1.46 Å [WT73] and the layer spacing is 3.35 Å [AF74]. For the first neighbour distance also the value 1.42 Å is referenced [AF74], but the potential used in this simulation is fitted to the value given first.

![Figure 3.3: Layer structure of graphite with hexagonal elementary cell.](image)

For simulations two crystal sizes have been used.

- 103.66 Å x 104.94 Å x 20.09 Å containing 28098 atoms
- 129.94 Å x 130.23 Å x 46.87 Å containing 93236 atoms

The choice of crystal sizes has been limited by the available computing power.
3.4 The structure of the diamond crystal

In diamond a $sp^3$ hybridization takes place. Therefore, the atoms arrange in a tetrahedral shape, each one being at the centre of a tetrahedron with its four nearest neighbours placed on the vertices of the tetrahedron. The resulting crystal is an fcc lattice with a two atom base at $(0,0,0)$ and $(\frac{a}{2}, \frac{a}{2}, \frac{a}{2})$ with the lattice parameter $a$ equal to 1.78 Å [Kit91]. For the elementary cell see figure 3.4.

![Elementary cell of diamond with tetrahedron like bonds.](image)

For the diamond simulations only one crystal size has been used but in two different orientations $\{010\}$ and $\{111\}$.

- $102.96 \, \text{Å} \times 102.96 \, \text{Å} \times 21.30 \, \text{Å}$ containing 42811 atoms in $\{010\}$
- $102.96 \, \text{Å} \times 102.96 \, \text{Å} \times 21.30 \, \text{Å}$ containing 41586 atoms in $\{111\}$

The diamond crystal size is roughly the same as the small graphite crystal. However, diamond is much harder and contains more atoms in the same volume.
3.5 The interaction model for the carbon system

Many potentials have been developed to deal with covalent bonded materials. Among these the one suggested by Tersoff [Ter88a, Ter88b, Ter89] is reasonably well accepted for non-conjugated systems. However, despite giving a good description of the covalent diamond and graphite intralayer forces it does not include the weak van der Waals forces between different layers in graphite. Therefore different modifications of the Tersoff potential have been developed. In this work two of them are investigated, the one brought forward by Nordlund [NKM96] and the one brought forward by Smith and Beadmore [SB96]. Both of them use the Tersoff potential at its core and add an extra term to describe the interlayer force.

The form of the Tersoff potential used for diamond and graphite has the following analytical structure.

\[ V_T(r_{ij}, \theta) = f_c(r_{ij}) \left( Ae^{-\lambda r_{ij}} - b_{ij} Be^{-\mu r_{ij}} \right) \]  \hspace{1cm} (3.5)

Hereby \( r_{ij} \) means the distance between atom \( i \) and \( j \). \( Ae^{-\lambda r_{ij}} \) gives a repulsive part and \( Be^{-\mu r_{ij}} \) gives an attractive one. \( b_{ij} \) represents a multi-body term which takes the environment of \( i \) and \( j \) into account and therefore the angle \( \theta \). The function \( f_c \) takes care of a smooth cut-off. For a detailed description and values of the parameters see appendix B.2.

To describe the graphite, additional terms are used. In the Nordlund case this is defined as following.

\[ V_G(r_{ij}, \phi) = \phi_3(G_{ij}) \left( V_{c0} - \left( e^{-\Delta(r_{ij} - c_0)} - 1 \right)^2 \right) \]  \hspace{1cm} (3.6)

Definition of \( r_{ij} \) is as above. \( \phi_3(G_{ij}) \) represents the multi-body term including the angle \( \phi \). For details, cut-off and parameters see appendix B.3.

Because of the inner cut-off, the potential is not continuous in the first derivative. The potential is cut when it reaches zero but the first derivative is particular high at this point (step approach of the zero point). Because the force
is calculated as the first derivative of the potential it means that it vanishes from a relative high value to null. Anyway, the potential is tested, because it is faster than the Smith potential and the influence of the discontinuities can be explored.

The formulation of the Smith interlayer term is of Lennard-Jones (LJ) type.

\[ V(r_{ij}) = V_e \left( \left( \frac{r_e}{r_{ij}} \right)^{12} - 2 \left( \frac{r_e}{r_{ij}} \right)^6 \right) \]  \hspace{1cm} (3.7)

\( V_e \) represents the energy and \( r_e \) the distance at equilibrium. The LJ potential is fitted with a quadratic spline to the Tersoff over the area were the Tersoff cut-off function acts. On the long range end the LJ potential is cut smoothly in a way that distant atoms in one layer give no addition to the interlayer force but distant atoms in different layers do. Therefore the neighbour list is checked to determine if two atoms are connected by covalent bonds which indicates them as being in one layer. For details see appendix B.4.
Part II

Results and Conclusion
Chapter 4

Simulation results

As mentioned earlier, there have been two potentials tested for the graphite simulations. The comparison of these should show the effect caused by the interlayer terms. Also, results are shown for different simulation times and, therefore, different interface velocities. This makes it possible to predict the influence of the time changes and therefore, enables one to judge the value of the results compared to experiments. For diamond there will be two surfaces tested, \{010\} and \{111\}. Results on planar forces and energy behaviour are also given. For the colour pictures the distance between each atom's current and initial position has been calculated and normalized with the nearest neighbour distance. With increasing distance colours range from blue to red.

4.1 Results for graphite with the Nordlund potential

First, the results for graphite with the Nordlund potential are presented. Hereby two series have been carried out. One for a crystal of 103.66 Å x 104.94 Å x 20.09 Å containing 28,098 atoms and one for a crystal of 129.94 Å x 130.23 Å x 46.87 Å containing 93,236 atoms. The first one is referred to as the 'small crystal' and the latter one as the 'big crystal'.
4.1.1 Small crystal

Figures 4.1-4.3 show the force-distance curves for the Nordlund potential for the small crystal with 5, 10, 50 ps simulation times respectively. In all cases the tip indents to a maximum depth of 8 Å. Generally every curve gives a hysteresis profile. Also every curve shows a zigzag line shape overlapped with bigger fluctuations, mostly at higher depths and at the same position for each of the different time simulations. The maximum force is roughly 70 eV/Å in all cases. However, the slope of the curve is slightly different for the different time values. With an increase of the time the hysteresis gets narrower. Also the shape of the dips at high indentation values gets narrower and appear almost like discontinuities in the curves.

Figure 4.4-4.9 show the side views of the lattice at half time and at the end for all three simulation simulations. The pictures at half time show similar behaviour for all three cases. Strong single atom displacement occurs only close to the interface and is nearly equal for all three simulations. The important difference is that the areal distortion increases with the higher time values. Areal distortion in this context means that there is displacement in a wide area even far away from the interface. Also this displacement does not vary much for neighbouring atoms and it is generally on a small scale. With increasing time this areal distortion covers a bigger area. The pictures at the end of the simulation are more different. For 5 ps there seems to be some remaining distortion between the 1st and 2nd layer. For 10 and 50 ps the lattice returns to its initial state with just small areal distortion left. Therefore, it shows complete elastic behaviour.

A few more pictures are shown in figures 4.10-4.13. The top layer of the lattice can be seen at half time and at the end for 5 ps and 50 ps. The pictures for 10 ps are identical to the 50 ps pictures. In the half time results, the shape of the tip is mirrored in the surface distortion. Also it can be seen how the atoms move apart from each other without destroying the hexagonal structure. This also
indicates that the deformation is an elastic process. Remarkably there is nearly no difference for the different simulations. Only at the edge of the distortion is there a slight change in the deformation of the hexagons. In the end picture, the 5 ps simulation stands on its own. It shows a remaining damage which could already be seen on the side views. Again the 10ps and 50 ps simulations show full recovery.

The lattice behaviour behind the pictures can be explained straightforwardly. While indenting, the tip pushes all atoms inside the cut-off range in the direction of its motion. The atoms try to remain in their crystal structure and therefore, develop a resisting force against the interface. With deeper penetration the distortion and so the resisting force increases. Also the first atoms which have moved transmit the force to atoms further away which have not yet seen the interface.

With the extraction of the interface the potential of the crystal tries to put the atoms back to their original position. However, there is a certain time shift between the new interface position and the corresponding force. The lattice needs a reaction time to adjust to the new interface position (the interface moves faster than the layers can relax). Therefore, the force distance curve is lower than during indentation and so the complete process forms a hysteresis. Hysteresis also comes from plastic behaviour but the 10 ps and 50 ps pictures show complete elastic behaviour. This also explains why the hysteresis gets narrower with increasing time. The time resolution is better so the reaction of the crystal is better represented.

This resolution effect may also be the reason for the change in the dips at deeper penetration. The idea behind this is, that atoms move so far away from each other that they do not see each other any more in terms of potential cut-off. Therefore, the interface sees in fact a lower force because the lattice structure is not as strong as at the begging. In reality the interface would increase its speed at this point, but this is not possible in the present interface model.

The explanation for the zigzag shape is more in the simulation technique. Its origin lies in the discontinuities of the potential. Therefore, this is later to be
compared with the van der Waals results to see if this speculation holds.
The simulation time clearly has an effect on the results. The longer ones suggest
an elastic behaviour which would go together with experiments for low depths
(even not as low as here). Shorter simulation times give the possibility of plastic
deformation and permanent atom displacement.

4.1.2 Big crystal

Figures 4.14-4.15 show the force-distance curves for a 15 Å deep penetration
into the big crystal. A hysteresis is still seen. With about 160 eV/Å the main
force is much higher than for the small crystal with lower impact. The hysteresis
is much larger. Also for the 5 ps run it is even larger than for the 10 ps run. A
zigzag line shape is still observed.

Figures 4.16-4.19 present the side view of the respective simulations. The half
time pictures look very similar to each other. On the top layer it can be seen that
the 5 ps simulation causes a wider deformation. Compared to the small crystal
the damage zone is much bigger. The end pictures show that in both cases
the lattice does not recover. The remaining distortion is somewhat different for
the two time values and seems to consist of areal distortion and single atom
displacement close to the interface location.

Figures 4.20-4.21 give the top view of the big crystal for 10 ps. The half time
picture again mirrors the interface. The image is of course much bigger than
with the small crystal. The end position shows the remaining damage which
lacks total symmetry but still partly preserves the shape of the interface. The
picture for the 5 ps case shows exactly the same and is therefore not presented.

It has been mentioned that the simulation time and therefore the interface
velocity is an important factor. The deeper impact with the bigger crystal
leads to a greater distance for the interface to move. With this big crystal,
it is not clear how much of the remaining damage is due to the speed of the
CHAPTER 4. SIMULATION RESULTS

simulation. This can only be answered in detail when computing power allows longer time scales to be simulated.

The larger width of the hysteresis in the force-depth curves can be explained by the motion of more atoms in deeper layers and therefore a longer relaxation time is required than for the smaller simulations. The wider range of the impact influence is clear to see. The interface is moving deeper into the bulk and therefore, acts with a wider cross section. Obviously the damage must extend over a wider area. Both the side and top views show this behaviour. To compare the simulations it is also possible to calculate the total cross-sectional area of tip involved in the interaction with the substrate. The total cross-section increases by a factor of 3.3 between the small and large crystal sizes. This is calculated using a value of $h$ which is measured from the original height of the undisturbed surface (see figure 3.2). To calculate the interaction zone the number of atoms which have moved more than half the nearest neighbour distance can also be evaluated. This number acts then as a representation of the size of the damage zone. For the smaller crystal there are 5623 atoms under this criteria for the big crystal 19,092. This leads to a factor of roughly 3.4. This corresponds approximately with the change in cross-sectional area. It also indicates that for the Nordlund potential the large movements of atoms are confined to a region close to the interface. Thereby, the atom displacements reproduce the interface and its size quite well. The last point is also supported by the half way pictures of the top view see figure (4.20).
CHAPTER 4. SIMULATION RESULTS

Figure 4.1: force-distance curve, Nordlund graphite, small crystal, 5 ps

Figure 4.2: force-distance curve, Nordlund graphite, small crystal, 10ps

Figure 4.3: force-distance curve, Nordlund graphite, small crystal, 50ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.4: side view, half time, Nordlund graphite, small crystal, 5 ps

Figure 4.5: side view, full time, Nordlund graphite, small crystal, 5 ps
Figure 4.6: side view, half time, Nordlund graphite, small crystal, 10ps

Figure 4.7: side view, full time, Nordlund graphite, small crystal, 10ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.8: side view, half time, Nordlund graphite, small crystal, 50ps

Figure 4.9: side view, full time, Nordlund graphite, small crystal, 50ps
Figure 4.10: top view, half time, Nordlund graphite, small crystal, 5 ps

Figure 4.11: top view, full time, Nordlund graphite, small crystal, 5 ps
Figure 4.12: top view, half time, Nordlund graphite, small crystal, 50 ps

Figure 4.13: top view, full time, Nordlund graphite, small crystal, 50 ps
Figure 4.14: force-distance curve, Nordlund graphite, big crystal, 5 ps

Figure 4.15: force-distance curve, Nordlund graphite, big crystal, 10ps
Figure 4.16: side view, half time, Nordlund graphite, big crystal, 5 ps

Figure 4.17: side view, full time, Nordlund graphite, big crystal, 5 ps
Figure 4.18: side view, half time, Nordlund graphite, big crystal, 10ps

Figure 4.19: side view, full time, Nordlund graphite, big crystal, 10ps
Figure 4.20: top view, half time, Nordlund graphite, big crystal, 10 ps

Figure 4.21: top view, full time, Nordlund graphite, big crystal, 10 ps
4.2 Results for the graphite with van der Waals potential

For the van der Waals potential the same variety of simulations has been carried out, using the same crystal sizes (see chapter 4.1). Again the same terminology for small and big crystals is used.

4.2.1 Small crystal

Figures 4.22-4.24 show the force-distance curves for the small van der Waals crystal for 5, 10, 50 ps simulation times respectively. Again, they show a hysteresis. The maximum force is smaller, 42 eV/Å in the 50 ps case and 50 eV/Å for 5 and 10 ps. The zigzag in the line shape has mainly disappeared. One dip at about 7 Å is still visible, but only in the 5 and 10 ps case. For the 50 ps case the curve is a smooth hysteresis. In general the hystereses are smaller and the 5 and 10 ps pictures show some bumps in the extraction curve.

Figures 4.25-4.30 present the side views. It is clear to see that the areal distortion increases with the higher time values. Also compared to the Nordlund potential the zone is bigger. It is interesting that the extraction of the tip leads to recovery of the lattice in all 3 cases.

Figures 4.31-4.34 show the top views. The half time results bring up the mirrored image again. But there is an interesting characteristic. The opening at the bottom of the dip is smaller with the 50 ps simulation. The 5 ps and 10 ps simulations look the same, so only the 10 ps case is given here. The end position shows again full recovery for all time values.

In principle the action is the same for both potentials. The van der Waals potential obviously estimates the interface force as a smaller value, so the lower maximum force emerges. The cause for the hysteresis stays the same. However, the hystereses are smaller than in the Nordlund case. There may be two
reasons for this. First, the lower interlayer force of the potential causes a lower shift during the reaction time of the lattice. Second, the discontinuities in the Nordlund potential create an amplification of the shift. This is hard to prove but discontinuities can lead to steps in the force calculations which will give a similar behaviour to the reacting time.

The dip at approximately 7 Å still can be explained with the model already mentioned (no adjusting in interface velocity). It is interesting that it disappears in the 50 ps simulation. The reason is twofold. The longer time gives a better resolution and the van der Waals potential generally describes the force closer (no discontinuities). This also indicates that with 50 ps (corresponding to an average interface velocity of 48 m/s) a threshold is overcome for which the speed of the interface allows a realistic description of the simulation. On the other hand this would mean that there are always discontinuities for calculations under 50 ps. In the Nordlund case the discontinuities of the potential have made it impossible to see this effect. Also, the bigger areal distortion for the van der Waals means that the layers react on a wider scale. The binding is more smooth and this may also contribute to the smoother force-distance curves.

The absence of the zigzags clearly reflects the continuous behaviour of the van der Waals potential compared to the Nordlund potential. So the zigzags can be explained as a discontinuity effect.

For the bumps on extract no explanation has been found yet.

4.2.2 Big crystal

Figures 4.35-4.36 give the force-distance curves for the big crystal with the van der Waals potential. The hystereses are smaller than with the Nordlund case but bigger than for the small crystal. The maximum force is about 100 eV/Å. There is no zigzag line shape but dips on the indenting part of the curve are clear to see.
Figures 4.37-4.40 show the side views. Compared to the small crystal the differences are similar to the Nordlund potential. The distortion is much bigger and slightly wider on the surface layer for 5 ps. The end positions show different remaining damages which are smaller than in the Nordlund case and consist more of areal distortion.

Figures 4.41-4.42 give the top views. Again, 5 ps and 10 ps are the same and so only the 10 ps picture is shown. The big mirror image of the interface at half time can be seen and the unsymmetric remaining damage at the end of the simulation.

The pictures of the big crystal give the chance to observe the following situation. The results show the strong time effect of the deep impact simulations (but without the discontinuity effect of the Nordlund potential). The force-distance pictures show a similar distorted hysteresis as the 5 ps and 10 ps pictures of the small crystal. The fluctuations must be due to the time effect. The Nordlund results add an additional distortion above this time effect. It is therefore postulated that most of the distortion in the Nordlund case is a potential effect.

For the van der Walls case, again a comparison of the size of the damage zone is done via counting the atoms. The small crystal has 5274 atoms in the zone, the big one 33,980. This lead to a factor of roughly 6.4. While the lower value corresponds with the Nordlund case the value for the big crystal is much higher. This can be explained by the less close adjustment of layers to the interface in the van der Waals potential. The lower binding keeps the layer further away from the interface, therefore, more atoms are in the damage zone.
CHAPTER 4. SIMULATION RESULTS

Figure 4.22: force-distance curve, vdW graphite, small crystal, 5 ps

Figure 4.23: force-distance curve, vdW graphite, small crystal, 10 ps

Figure 4.24: force-distance curve, vdW graphite, small crystal, 50 ps
Figure 4.25: side view, half time, vdW graphite, small crystal, 5 ps

Figure 4.26: side view, full time, vdW graphite, small crystal, 5 ps
Figure 4.27: side view, half time, vdW graphite, small crystal, 10 ps

Figure 4.28: side view, full time, vdW graphite, small crystal, 10 ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.29: side view, half time, vdW graphite, small crystal, 50 ps

Figure 4.30: side view, full time, vdW graphite, small crystal, 50 ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.31: top view, half time, vdW graphite, small crystal, 10 ps

Figure 4.32: top view, full time, vdW graphite, small crystal, 10 ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.33: top view, half time, vdW graphite, small crystal, 50 ps

Figure 4.34: top view, full time, vdW graphite, small crystal, 50 ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.35: force-distance curve, vdW graphite, big crystal, 5 ps

Figure 4.36: force-distance curve, vdW graphite, big crystal, 10ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.37: side view, half time, vdW graphite, big crystal, 5 ps

Figure 4.38: side view, full time, vdW graphite, big crystal, 5 ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.39: side view, half time, vdW graphite, big crystal, 10ps

Figure 4.40: side view, full time, vdW graphite, big crystal, 10ps
Figure 4.41: top view, half time, vdW graphite, big crystal, 10 ps

Figure 4.42: top view, full time, vdW graphite, big crystal, 10 ps
4.3 Results for the diamond

For diamond there has been only one crystal size examined, 102.96 Å x 102.96 Å x 21.30 Å. It has been done for two surfaces, {010} with 42,811 particles and {111} with 41,586 particles.

4.3.1 {010} surface

Figures 4.43-4.45 show the force-distance curves for the diamond {010} surface with a 4 Å penetration depth. The maximum force is different for each simulation time, 170 eV/Å, 150 eV/Å, 130 eV/Å respectively. All pictures give a hysteresis profile with the 5 ps and 10 ps ones being somehow zigzag shaped, while the 50 ps result gives a narrower hysteresis, consisting of smooth portions with several clear steps. At these steps the force drops down suddenly and after that the curve continues as before on a lower level.

Figures 4.46-4.51 give the side views. Generally the distortion is less clear to see than with the graphite pictures. Also it is not a layer by layer action as in graphite, due to the different structure of diamond. There is some areal distortion which increases with the slower simulation. Above these areal distortions there are single atom displacements which form different structures close to the surface (a graphite ring for 5 ps, an adatom for 50 ps). This damage remains stable at the end of the simulation, while the areal distortion decreases and for the 50 ps case vanishes.

Diamond is a much harder material than graphite. Therefore higher force values are expected. The interesting point is that the maximum values are different for each time value. This indicates that time effects are even more crucial than with the graphite.

The faster simulations give similar hystereses as seen before in the 5 and 10 ps graphite simulations with the curves exhibiting zigzags and dips. Completely different is the comparison with the 50 ps case. A line shape almost completely
free from zigzags is interrupted by sharp steps. If it is assumed that these steps have a similar origin than the dips in the graphite pictures they go together with atoms leaving the range of the tetrahedron bonds. The fact of these effects being so sharp would than be characteristic for the diamond hardness. Since there is remaining damage at the end for all time values this seems quiet reasonable. Also the remaining damage for the 50 ps case is the most clear structure without any areal displacement left.

Diamond has not as flexible a layer structure as graphite. Therefore, there are more displacements of single atoms close to the interface which allow permanent displacement. This goes in line with diamond being a stiffer material.

4.3.2 \{111\} surface

Figures 4.52-4.54 show the force-distance curves for the diamond \{111\} surface. In principle they are similar to the \{010\} face but the maximum force is lower, 135 eV/Å, 120 eV/Å, 115 eV/Å for 5, 10 and 50 ps respectively. The 50 ps case has less steps than in the \{010\} simulation. At the start of the \{111\} simulations before the tip reaches the surface, the surface reconstructs. This aspect is discussed in more detail in chapter 4.7.

Figures 4.55-4.60 present the side views. The areal distortion increases with time while the surface damage seems to decrease. General there are less atom displacements to see than with \{010\} face. Also there is no remaining damage for the 50 ps case and is more areal for the others compared to \{010\}.

Figures 4.61-4.64 show the top view for 5 ps and 50 ps. The damage looks different than for graphite. However the shape of the indenter can be seen in the half time pictures, more clearly in the 50 ps simulation. Also for the longer simulation there is a greater areal distortion. The healing from half to full time seems to be less regular with the faster simulation which would be consistent with the remaining damage in this case. On the other hand the slow simulation
shows full recovery.

Compared to \{010\} there are lower maximum force values. This is not realistic because the \{111\} surface is experimentally observed to be harder. The surface used in the simulation is not reconstructed. In reality such a surface would either reconstruct or be covered by an adsorbed layer such as hydrogen. This would create a difference in the calculations and could be improved by a further refinement of the model.

It is interesting to see that there are less steps in the 50 ps force-distance curve than with \{010\}. Also the 50 ps \{111\} crystal recovers almost completely. Even the 5 ps and 10 ps pictures show less displacements than the \{010\} results. Particularly the single atom displacements are gone which indicates again that they are a surface effect (\{010\} - \{111\}), while the area distortion is a time effect. The behaviour is closer to the van der Waals graphite results than the \{010\} surface (the \{111\} surface looks from above similar to the graphite perpendicular to layers).

Because the unreconstructed \{111\} surface shows a more elastic behaviour than the \{010\} surface which is not realistic, it would be an interesting test to develop a better reconstruction model and then simulate the same procedure again.
CHAPTER 4. SIMULATION RESULTS

Figure 4.43: force-distance curve, diamond \{010\}, 5 ps

Figure 4.44: force-distance curve, diamond \{010\}, 10ps

Figure 4.45: force-distance curve, diamond \{010\}, 50ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.46: side view, half time, diamond \{010\}, 5 ps

Figure 4.47: side view, full time, diamond \{010\}, 5 ps
Figure 4.48: side view, half time, diamond \{010\}, 10ps

Figure 4.49: side view, full time, diamond \{010\}, 10ps
Figure 4.50: side view, half time, diamond \{010\}, 50ps

Figure 4.51: side view, full time, diamond \{010\}, 50ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.52: force-distance curve, diamond {111}, 5 ps

Figure 4.53: force-distance curve, diamond {111}, 10ps

Figure 4.54: force-distance curve, diamond {111}, 50ps
Figure 4.55: side view, half time, diamond \{111\}, 5 ps

Figure 4.56: side view, full time, diamond \{111\}, 5 ps
Figure 4.57: side view, half time, diamond \{111\}, 10ps

Figure 4.58: side view, full time, diamond \{111\}, 10ps
Figure 4.59: side view, half time, diamond \{111\}, 50ps

Figure 4.60: side view, full time, diamond \{111\}, 50ps
CHAPTER 4. SIMULATION RESULTS

Figure 4.61: top view, half time, diamond \(\{111\}\), 5 ps

Figure 4.62: top view, full time, diamond \(\{111\}\), 5 ps
Figure 4.63: top view, half time, diamond \{111\}, 50 ps

Figure 4.64: top view, full time, diamond \{111\}, 50 ps
4.4 Discontinuities and the interlayer term

It has been stated in chapter 3.5 that the Tersoff potential does not describe the interlayer forces in graphite. Therefore the additional terms are introduced (Nordlund, van der Waals). The Nordlund term exhibits some discontinuities which manifest themselves in the shape of the force-distance curves.

To demonstrate the effect of the interlayer terms a simulation for the small graphite crystal has been carried out over 50 ps using only the pure Tersoff potential. Figure 4.65 compares the results of the force-distance relationship with the results for the Nordlund and the van der Waals potential for the corresponding crystal and simulation time.

![Figure 4.65: force distance curves for three potentials, graphite, small crystal, 50 ps](image)

It is clearly seen that only the Nordlund potential gives the zigzag shape. It is concluded that the discontinuities in its interlayer term are responsible for this. Also the plane Tersoff shows that the force is much lower if there is no interlayer term. The different approaches for the interlayer terms have a marked difference in their force values. This shows that the interlayer term is important for the calculations and also underlines the point that the structural results from the previous sections strongly depend on this.
4.5 Planar forces

In all previous sections only the force perpendicular to the surface has been investigated. However the interface also experiences a force perpendicular to the direction of motion parallel to the surface of the crystal. This force can be described in terms of components in the direction of two cartesian axes in the plane of the surface which are termed x and y. For graphite the x-axis is parallel to the longer diagonal of the base plane of the hexagonal elementary cell which is shown in figure 3.3.

In figure 4.66 the force-distance curve in the x and y directions are presented for the small van der Waals graphite simulated over 50 ps. Figure 4.67 and 4.68 give the forces in the x and y directions for the diamond {111} surface simulated over 50 ps.

The scale on the force axis is far smaller than in the force distance curve of the previous sections. The contact point of the tip is at the origin and lies in the middle of the crystal surface. This is the reason for the appearance of negative force values which are just a question of direction. The interface experiences forces in the positive and negative x and y directions and most of the forces cancel each other out.

With the graphite the x force oscillates around zero with very low values. This shows that the contact point of the tip lies at a symmetric point towards the x direction and forces cancel each other out completely. The y curve does not have this symmetry. It extends to about 5 eV/Å and returns on a hysteresis. The tip is closer to atoms in the positive y direction and therefore experiences a stronger force from this side. However, the force stays far lower than in the perpendicular direction.

The two diamond pictures show no symmetry at all. The maximum force values extend to about 10 eV/Å. In the diamond there was more atom displacement at the surface. This may be the reason for the asymmetric behaviour albeit
with forces that are far smaller than in perpendicular direction.

These results are an additional verification of only small structural changes in the crystals. It would be expected that large structural changes would be asymmetric and show a larger effective force exerted in the x-y plane on the tip.
Figure 4.66: force distance curve in $x$ and $y$, vdW graphite, small crystal, 50 ps

Figure 4.67: force distance curve in $x$, diamond $\{111\}$, 50 ps

Figure 4.68: force distance curve in $y$, diamond $\{111\}$, 50 ps
4.6 Energetic results

During the simulations, the kinetic and potential energy of the atoms in the crystal are recorded. These can be used to describe some general features of the simulation.

![Figure 4.69: total energy, vdW graphite, small crystal, 50ps](image)

Figure 4.69 shows the total energy for the graphite van der Waals simulation with the small crystal over 50 ps. The energy is normalised with the potential energy in the first step.

It is clear to see how energy is added to the system during the indentation. Interestingly the peak value is achieved slightly before the half time which represents the deepest impact. The end value stays a little higher than the start. This is reasonable because at the end there was still areal distortion to see and so there is still energy stored in the system. The total energy added to the system comes up to 130 eV. If this is seen in relation to the total number of 28,098 particles in the crystal it is clearly not enough to break many bonds. This low value is also a verification that the damping dissipates the energy in a reasonable way.

The potential energy is not shown but has the same shape as the total energy.
curve. This is because the kinetic energy is very small. Figure 4.70 shows the kinetic energy. Note that the scale on the energy axis is much lower than for the total energy curve.

![Figure 4.70: kinetic energy, vdW graphite, small crystal, 50ps](image)

The overall shape of the kinetic energy curve also correspond to the shape of the total energy. The maximum in the kinetic energy curve is also found close to the point of deepest impact. Interestingly the shape of the curve exhibits oscillations. This implies that there is also oscillation of the atoms during their displacement by the interface.

![Figure 4.71: total energy, diamond {111}, 50ps](image)
To compare the energy results with diamond, the total energy for the \(\{111\}\) surface with a simulation time of 50 ps is presented in 4.71. Note that the scale is different than with graphite.

The main feature is that the system loses potential energy at the start of the simulation. After that there is a similar behaviour to graphite. The minimum point energy occurs after about 5 ps and then energy is added to the system reaching a maximum at approximately half-time and then is dissipated again. The strong energy reduction at the start is explained by relaxation of the surface. While the tip is approaching the surface relaxes under the influence of its own potential, thereby trying to reach the minimum potential energy configuration. After the tip is close enough its influence takes over and creates the more usual behaviour. The total energy transferred to the system during this state is about 250 eV. This is higher than with the graphite and can be understood because diamond is harder and the indentation therefore results in a stronger potential energy rise.

Again the potential energy shows the same shape as the total energy curve because the kinetic energy acts on a much smaller scale. Figures 4.72 - 4.73 show the kinetic energy. Two pictures are chosen to illustrate the effects over different scales.

Figure 4.72 is shown on a large scale. The kinetic energy at first is rather high and oscillates. This corresponds with the relaxation process which involves the largest movement of atoms and therefore kinetic energy increase. After that the energy is dissipated from the system faster than kinetic energy is added through the relaxation process. Figure 4.73 shown on a small scale emphasises this. Interesting are the 3 steps which can be seen in this curve. This may be indicative of atoms leaving their original sites and rearranging.
Figure 4.72: kinetic energy, diamond \{111\},
50ps

Figure 4.73: kinetic energy, diamond \{111\},
50ps
4.7 Reconstruction

It has already been mentioned that the diamond \{111\} surface is not stable. In reality it relaxes and this process is not considered in the simulations.

To improve this a simple model to simulate the relaxation was introduced. The crystal dynamics are calculated according to the MD process but without any indentation. The atoms should then move towards the minimum positions of the potential energy. Every 10 time steps the velocities are set to zero to suppress oscillation around the minimum positions. A simulation for this was running for 10 ps.

Figures 4.74 - 4.76 give the potential, kinetic and total energy respectively. It is to be noted that the energy axis expands over the same range in all three pictures. The total energy is normalised to the potential energy of the first step.

At first there is some sort of start oscillation to see. After that the potential energy reduces very quickly and then comes into a state of stability. This goes together with the atoms moving towards the minimum energy positions. The kinetic energy behaves in the same way. This also indicates that the atoms reach minimum energy positions and therefore no longer experience a strong movement. The dissipation of energy from the system comes from the damping process and the rescaling of the velocities. This is also expressed in the total energy.

The model above may lead to a minimum energy position but this still may not be the global relaxation position. This may be in another minimum arrangement. Notwithstanding this, the relaxed surface from the model above was used as a start configuration for a simulation over 50 ps. The results did not change substantially from the ones already obtained. This suggests that further work should be carried out to model the relaxation process.
CHAPTER 4. SIMULATION RESULTS

Figure 4.74: potential energy reconstruction

Figure 4.75: kinetic energy reconstruction

Figure 4.76: total energy reconstruction
Chapter 5

Experimental results

To judge the value of the simulations it is necessary to compare them to experiments. Therefore results are presented which have been obtained by Richter et al. [RRS+99].

The experiments were performed with the Hysitron Nanoindenter Triboscope. A diamond pyramid was used as the indenter which has three faces and an 90° angle. The {111} surface lies parallel to the surface of the sample. This corresponds to the geometry used in the simulations. However there is some rounding of the tip due to continual wear so after some indentations the angle is no longer 90°. This has an effect particular with small indentation depths. During the experiment a force is applied to the tip and according to the maximum value of this force, the tip moves to a maximum depth into the bulk. After extraction the surface is analysed with the same tip acting as a SFM.

5.1 The shape of the indentation

Figure 5.1 shows an SFM image of the indentation area on an aluminium substrate with a maximum load of 1426 μN. The average side length for the triangular shape is 1.77 μm. Using the ideal tip geometry as described in Chapter
CHAPTER 5. EXPERIMENTAL RESULTS

Figure 5.1: SFM image of a plastic deformation in Al showing a triangular cross section. The sides are approximately 1.77 \( \mu m \).

3:1 leads to an indentation depth of 723 \( nm \). The rounding of the tip gives a lower depth which was measured as 418 \( nm \).

Interestingly for the comparison with the simulation is the clearly visible triangular shape. The simulation top views of the graphite crystal also showed triangular surface distortion. However, the simulation pictures are taken with the interface still inside the bulk. In the case of plastic deformation the shape remains at the end of the simulation.

Figure 5.2: Inverted SFM image of plastic deformation in Al.
Figure 5.2 is a three-dimensional inverse image of the indentation region. It emphasises the result of the previous picture and the pyramidal shape is again in good similarity with the simulation top views.

### 5.2 Calculating mechanical properties

It is possible to calculate the hardness and the elastic moduli from force-distance curves using continuum models. Figure 5.3 gives a standard force distance hysteresis with the most important labeling.

\[ h_{\text{max}} \text{ denotes the maximum indentation depth, while } h_p \text{ stands for the penetration depth at which the triangular cross section } A_c \text{ is taken for the calculations. Increasing means during indentation while decreasing means on retreat of the interface. } F_{\text{max}} \text{ represents the maximum force applied. The dashed line from } h_p \text{ to the top of the curve gives the slope } \frac{dF}{dh} \text{ at the maximum indentation. } \delta \text{ is called the elastic recovery.} \]

Nano-hardness \( H_N \) is defined by \([\text{OP92, WSKP99}]\)

\[
H_N = \frac{F_{\text{max}}}{A_c}
\]  

(5.1)
and the effective Young’s modulus $E$ is defined by

$$E = 0.5 \frac{dF}{dh} / \sqrt{\frac{A_c}{\pi}}$$

(5.2)

After Hertz [Her82] $h_p$ is defined by $h_f + 0.5(h_{max} - h_f)$ and $\delta = h_{max} - h_p$. Also $\frac{E_{max}}{A_c} = \frac{3}{2} \frac{E_{max}}{A_c}$ because in the ideal case $F$ is proportional to $\delta^{\frac{3}{2}}$. In the case of no plastic deformation $\delta$ is equal to the full penetration depth.

The Herz model does not really apply to the simulations presented here because the indentation region is far too small to approximate the continuum model.

### 5.3 Experimental force-distance curves

![Experimental force-distance curve](image)

Figure 5.4: Experimental force-distance curve for diamond.

For diamond the applied forces in the experiment were raised to 3350 $\mu$N and resulted in complete elastic behaviour. Indentation depths were very small because of the hardness of the material and no sign of plastic deformation could be seen at the end of the indentation.

Figure 5.4 gives an experimental force-distance curve for a diamond {111} surface. Analysing the curve showed a dependency of the form $F = const \times \delta^m$. With $m$ taking an value of 1.6 instead the theoretical value of 1.5. Note that the elastic recovery $\delta$ is the full indentation depth for diamond and was obtained
from the diagram as 36 nm. Using this and the model from above it results in an elastic moduli for the \{111\} surface of 1137 GPa. For this calculation the rounding of the tip and the mechanical character of the tip were also taken into account. For the nanohardness the value was 117 GPa.

Figure 5.5: Experimental force-distance curve for graphite, elastic behaviour.

Figure 5.6: Experimental force-distance curve for graphite, plastic behaviour.

Figure 5.5 show a force distance curve for graphite with full elastic behaviour. This is valid as long as the force does not extend over 1240 μN. If higher force values are applied the curve is at first the same but at about 1240 μN the force drops to zero representing plastic behaviour. Thereby a sudden breakthrough
appears with several layers breaking and after this the curve resumes its previous form. The picture is shown in figure 5.6.

Analysing figure 5.5 it is found that $m$ is about 1.4 and $\delta = 202$ nm. This gives an elastic moduli of $10.5 \, GPa$ and a nanohardness of $2.35 \, GPa$.

### 5.4 Comparison

The experiments act on much higher force and depth values. It is therefore difficult to make a direct comparison between the force distance curves because the experimental ones do not show detail enough to do so.

Nevertheless an attempt has been made to compare the two by calculating the elastic moduli from the simulated curves. The results have to be taken with great care because the Hertz model from above does not really apply to the dimensions used in the simulations.

For graphite the 50 ps simulations were used with the plane Tersoff potential, the Nordlund potential and the van der Waals potential. For diamond the $\{010\}$ and the $\{111\}$ surface with 50 ps simulation time are used. Because the extraction is done too fast in the simulation for the crystal properly to relax all calculations have been performed using the decreasing and increasing part of the force-distance curve.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Increasing</th>
<th>Decreasing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tersoff</td>
<td>55 $GPa$</td>
<td>96 $GPa$</td>
</tr>
<tr>
<td>Nordlund</td>
<td>184 $GPa$</td>
<td>294 $GPa$</td>
</tr>
<tr>
<td>van der Waals</td>
<td>108 $GPa$</td>
<td>162 $GPa$</td>
</tr>
<tr>
<td>${010}$</td>
<td>726 $GPa$</td>
<td>953 $GPa$</td>
</tr>
<tr>
<td>${111}$</td>
<td>629 $GPa$</td>
<td>1015 $GPa$</td>
</tr>
</tbody>
</table>

The previous table gives the values obtained by the calculations. If they are compared to the experimental values given in the previous section it can be seen that the graphite values are about one magnitude too high. With the diamond
the \{111\} value is in about the same range as in the experiments. As mentioned the Hertz model does not apply to the system of the simulations, so a comparison can never be exact. Nevertheless the calculations are an interesting exercise to get an idea how the atomistic simulations behave in the continuum limit.
Chapter 6

Conclusion, Criticism

6.1 Conclusion

A basic model for nanoindentation into carbon materials has been set up. The atomistic structure of the tip has not been taken into account, it is treated as a purely hard wall (ZBL potential). Investigations have been carried out for graphite using three different potentials (pure Tersoff, Nordlund, van der Waals) to describe it and for diamond examining two different surfaces ($\{010\}$, $\{111\}$). To analyse influence of penetration depth two crystal sizes with different impact depths (8 Å, 15 Å) have been simulated for the graphite. The diamond surfaces have not been reconstructed but for visualisation purpose a movie has been created for the $\{111\}$ surface (see appendix C). To investigate the influence of the interface velocity different simulation times (5 ps, 10 ps, 50 ps) have been used. To get comparison with reality some experimental pictures have been put next to simulation pictures.
6.1.1 Graphite

All simulations resulted in force-distance curves which exhibited hysterises. They are narrower for slower simulations and for the van der Waals potential. In case of the Nordlund potential they are zigzag shaped because of discontinuities in the potential. Both effects together lead to a completely smooth curve for the 50 ps van der Waals simulation. Maximum force values are estimated higher for the Nordlund potential with about 70 eV/Å and lower for the van der Waals with between 42 and 50 eV/Å. Deeper impacts of 15 Å with a bigger crystal leads to a wider hysteresis. The simulation in this case is carried out at an even higher velocity and the force-distance curves are not smooth. Besides this the force values are higher, about 160 eV/Å, more than double the 8 Å value.

The binding of layers is stronger for the Nordlund potential and during the simulation the graphite layers do not move so much far from the interface. Areal distortion and single atom displacement can be observed. Single atom displacements are stronger with the Nordlund potential, deeper impacts and faster simulations, while areal displacement is dominant for the van der Waals potential, small crystals and slower simulations. Full recovery goes together with the cases where areal distortion is dominant, otherwise remaining damage occurs. For the Nordlund potential the atom displacement zone increases proportional to the cross-section of the interface involved. In the van der Waals simulation the displacement zone extends much further.

Surfaces at half simulation time mirror the shape of the indenter. Both potentials behave identical in this matter. The bigger crystal just leads to a bigger image. Surfaces at the end of the simulation show full recovery in the cases where areal distortion is dominant, with damage remaining otherwise.
6.1.2 Diamond

Even with a lower indentation depth force values are much higher for diamond. They are higher for \{010\} which is contrary to experiments. Also they vary quite a lot with simulation time. The diamond simulations seem to be more sensitive to time changes. The force-distance curves exhibit hystereses in all cases. They are smaller than for the graphite. They show some zigzags for fast simulations while the slow simulation is mainly smooth but with some steps. These are thought to go together with breaking bonds.

Damage behaviour is not as organised in layers as with the graphite. Areal distortion and single atom displacement are observed. Single atom displacement is stronger for faster simulations and for the \{010\} surface. Also the single atom structures obtained by this are much clearer to see and more frequent than with graphite. Areal parts of distortion recover while single atom displacements tend to remain at the end of the simulation. In these cases adatom structures can be observed at the end of the simulation.

Surface damage appears as an image of the indenter but not as clearly rendered as with graphite. But there seems to be the same tendency for recovering in the case of the slower simulations.

6.1.3 General

Impacts have been performed for much lower time, depth and force values than used in experiment. However, the basic features of elastic behaviour in low impact situations could be observed. For faster simulations, plastic effects occurred. These can at least give some ideas about what can be expected when real plastic deformation takes place. Considering this, great care has to be taken to use a realistic simulation time and therefore also a reasonable interface velocity.

Force distance curves could be simulated as hystereses and are quite realistic.
Damage occurred as single atom displacement and as areal distortion. The displacement of single atoms is strengthened by time effects in fast simulations. The areal distortion is more important in all cases where full recovery was achieved at the end of simulation. Therefore it seems to be the more realistic behaviour for elastic processes.

6.2 Criticism

Computer simulation is based on simplifying models. It always has to be considered how strongly reality is changed. In the present work it is obvious that the time scale is much lower than in reality. Therefore only low impact is simulated and the interface velocities are much higher than in reality. Current computer power does not allow one to use longer time scales or go to deeper depths. The latter would require bigger crystals which again would slow down the simulations. Despite this limitation many features of the experiments could be reproduced. The limitations in computer power are therefore only a delay in going to the full range of experimental values. The model itself should still apply.

The model for the diamond has to be changed to take the reconstruction of surfaces into account.

An interesting possibility would be to model the interface with an atomistic structure. By this it could be possible to look at atom-atom reactions between tip and surface.
Part III

Appendix
Appendix A

Damping

As mentioned earlier boundary conditions are introduced in form of a velocity proportional damping. The main point is to obtain a realistic value for the damping constant $\beta$ ([Hen97]).

To approximate this a damped harmonic oscillator is considered. The law of motion is as following:

$$ma = -kx - \beta v,$$  \hspace{1cm} \text{(A.1)}

where $a$ is the acceleration, $m$ the mass, $v$ the speed and $k$ the force constant of the potential. With $\omega^2 = \frac{k}{m}$ and $2\gamma = \frac{\beta}{m}$ it changes to:

$$a + 2\gamma v + \omega^2 x = 0.$$  \hspace{1cm} \text{(A.2)}

This is a linear homogeneous differential equation which permits different types of motion. One such form represents a single displacement and slow return to the initial position. In this case:

$$\omega^2 = \gamma^2 \quad \rightarrow \quad \beta = 2\sqrt{mk}.$$  \hspace{1cm} \text{(A.3)}

The damping constant can be obtained from $m$ and the force constant $k$. The potential of the oscillator is $V_0 = -\frac{1}{2}kx^2$. If this is fitted to the Tersoff potential
at the minimum energy point $k$ can be obtained. The result is:

$$\beta = 1.957 \times 10^{-12} \text{kg s}^{-1}. \quad (A.4)$$
Appendix B

Potentials

B.1 The ZBL potential and its parameters

The explicit form of the ZBL potential is as following.

\[ V_{ZBL}(r) = \frac{Z_1 Z_2 e^2}{4\pi \varepsilon_0 r} \sum_{i=1}^{4} c_i e^{-\frac{a_i}{a} r} \]  \hspace{1cm} (B.1)

with

\[ a = 0.46850 \frac{a_0}{Z_1^{0.23} + Z_2^{0.23}} \]  \hspace{1cm} (B.2)

Here \( Z_1 \) and \( Z_2 \) as the atom numbers of the particles involved, \( r \) is the interatomic spacing, \( e \) the electronic charge, \( a_0 \) is the Bohr radius and \( \varepsilon_0 \) the permittivity of free space. The parameters are as follows.

\[ c_1 = 0.02817 \quad d_1 = 0.20162 \]
\[ c_2 = 0.28022 \quad d_2 = 0.40290 \]
\[ c_3 = 0.50986 \quad d_3 = 0.94229 \]
\[ c_4 = 0.18175 \quad d_4 = 3.19980 \]
APPENDIX B. POTENTIALS

B.2 The Tersoff potential and its parameters

The form of the Tersoff for diamond and graphite has the following analytical structure.

\[ V_T(r_{ij}, \theta) = f_c(r_{ij}) \left[ A e^{-\lambda r_{ij}} - b_{ij} B e^{-\mu r_{ij}} \right] \]  \hspace{1cm} (B.3)

with

\[ b_{ij} = \chi (1 + \beta^n \zeta_{ij}^n)^{-1/2n} \]  \hspace{1cm} (B.4)

where

\[ \zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}) e^{\lambda^2 (r_{ij} - r_{ik})^2} \]  \hspace{1cm} (B.5)

\[ g(\theta_{ijk}) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos(\theta_{ijk})^2) \frac{d^2}{h^2}} \]  \hspace{1cm} (B.6)

also

\[ f_c(r_{ij}) = \begin{cases} 1 & r_{ij} < R \\ \frac{1}{2} + \frac{1}{2} \cos(\pi \frac{r_{ij} - R}{S}) & R < r_{ij} < S \\ 0 & r_{ij} > S \end{cases} \]  \hspace{1cm} (B.7)

Hereby \( r_{ij} \) means the distance between atom \( i \) and \( j \), \( r_{ik} \) the distance between \( i \) and \( k \). \( \theta_{ijk} \) represents the angle between \( i, j, k \) as seen from \( i \). The function \( f_c \) takes care of a smooth cut-off between \( R \) and \( S \). For carbon the parameters are as follows.

\[
\begin{align*}
A &= 1393.6 \text{ eV} & \beta &= 1.5724 \times 10^{-7} \\
B &= 346.7 \text{ eV} & n &= 0.72751 \\
\lambda &= 3.4879 & c &= 38049 \\
\mu &= 2.2119 & d &= 4.3483 \\
R &= 1.8 \text{ \AA} & h &= -0.57058 \\
S &= 2.46 \text{ \AA} & \lambda_3 &= \mu
\end{align*}
\]
APPENDIX B. POTENTIALS

B.3 The Nordlund extension and its parameters

The Nordlund extension is:

\[ V_G(r_{ij}, \phi) = \phi_3(G_{ij}) \left( V_{c0} - \left( e^{-l_4(r_{ij} - c_0)} - 1 \right)^2 \right) \]  \hspace{1cm} (B.8)

with

\[ \phi_3(G_{ij}) = \frac{-l_0}{1 + \left( \frac{G_{ij} - 3}{l_3} \right)^2} \]  \hspace{1cm} (B.9)

\[ G_{ij} = \sum_{k \neq i, j} \phi_1(\theta_{ijk})\phi_2(r_{ik}) \]  \hspace{1cm} (B.10)

\[ \phi_1(\theta_{ijk}) = \frac{1}{1 + \left( \frac{\cos \theta_{ijk}}{l_1} \right)^4} \]  \hspace{1cm} (B.11)

\[ \phi_2(r_{ik}) = \frac{1}{1 + \left( \frac{r_{ik} - r_{0}}{l_2} \right)^4} \]  \hspace{1cm} (B.12)

The definitions of \( r_{ij}, r_{ik} \) and \( \theta_{ijk} \) are as with Tersoff. \( V_G \) is cut off at a higher value of \( r_{M1} \) and at a lower value of \( r_{M0} = c_0 - \frac{\ln 1 + \sqrt{V_{c0}}}{l_4} \) (represents \( V_G(r_{ij}, \phi) = 0 \)). The parameters are as follows.

\[ l_0 = 0.0456 \text{ eV} \quad r_0 = 1.46 \text{ Å} \]
\[ l_1 = 0.07 \quad c_0 = 3.348 \text{ Å} \]
\[ l_2 = 0.21 \text{ Å} \quad V_{c0} = 2.33 \]
\[ l_3 = 0.15 \quad r_{M1} = 4.3 \text{ Å} \]
\[ l_4 = 1.94 \text{ Å}^{-1} \quad r_{M0} = 2.87 \text{ Å} \]

B.4 The cut-off function for the Lennard-Jones potential

In principle the same cut-off function as the with the Tersoff is used to check for covalent bonds.

\[ f_{c}^{tr}(r_{ij}) = \begin{cases} 
1 & : \ w_{ij} \leq 0 \\
\frac{1}{2} + \frac{1}{2} \cos(\pi w_{ij}) & : \ 0 \leq w_{ij} \leq 1 \\
0 & : \ w_{ij} \geq 1 
\end{cases} \]  \hspace{1cm} (B.13)
APPENDIX B. POTENTIALS

with

\[ w_{ij} = f_c(r_{ij}) + \sum_{k \neq i,j} f_c(r_{ik})f_c(r_{kj}) + \sum_{l \neq i,j,k} f_c(r_{ik})f_c(r_{kl})f_c(r_{lj}) \] (B.14)

and

\[ f_c(r_{ik}) = \begin{cases} 
1 & : r_{ik} \leq R_i \\
\frac{1}{2} - \frac{1}{2} \sin\left(\pi \frac{r_{ik}-R_i}{R_o-R_i}\right) & : R_i \leq r_{ik} \leq R_o \\
0 & : r_{ik} \geq R_o 
\end{cases} \] (B.15)

\( r_i \) is equal to 5.0 Å and \( R_o \) is equal to 5.5 Å. \( f_c \) is the same cut-off function as the Tersoff one. Therefore, \( f_{ij}^c \) has the effect of checking if \( i \) and \( j \) are connected by 3 covalent bonds. If so, the interaction does not count for the interlayer term.

In this work the checking takes place up to 5 covalent bonds, the extension to \( w_{ij} \) is just the addition of two more sums built in an appropriate way.
Appendix C

Movie

As mentioned earlier a movie has been created with a 4 Å impact on the diamond \{111\} surface using a simulation time of 50 ps. The start configuration was a \{111\} surface which has been reconstructed with the model from chapter 4.7 for a period of 5 ps. For the movie a picture was taken every 0.5 ps.

Figures C.1 - C.12 show the pictures obtained by this every 5 ps with the reconstruction period included. The interface is not pictured and the view point is straight above the contact point tip-surface. The direction of view is perpendicular to the surface focused on the contact point. The colours reflect the range over which the atoms have moved with blue representing no movement and red representing the largest movement.

It can be seen that during the reconstruction period, atoms start to move on a small scale all over the surface but no dramatic change to the structure appears. After that the crystal starts to react on a growing area centred around the contact point, thereby reflecting the indenting tip. During the retreat of the tip the crystal returns to its original arrangement with nearly no remaining distortion to see.
Figure C.1: \{111\}, 0 ps
Figure C.2: \{111\}, 5 ps
Figure C.3: \{111\}, 10 ps
Figure C.4: \{111\}, 15 ps
Figure C.5: \{111\}, 20 ps
Figure C.6: \{111\}, 25 ps
Figure C.7: \{111\}, 30 ps
Figure C.8: \{111\}, 35 ps
Figure C.9: \{111\}, 40 ps
Figure C.10: \{111\}, 45 ps
Figure C.11: \{111\}, 50 ps
Figure C.12: \{111\}, 55 ps
Part IV

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