The effects of atom pinning on hardness in molecular dynamics simulations.

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Abstract

Molecular Dynamics (MD) simulations were performed to find out if it was possible to adjust the hardness of a 100% iron simulation by attaching a proportion of atoms to their initial positions by means of springs. This was done by running one set without such 'pinned' atoms to find the inherent variability and then running a second set with a steadily increasing proportion of atoms pinned. The results for the repeated set are $18.7 \pm 1.3$ GPa showing that there is inherently a certain amount of variation. The results for the main set show a much larger change as a result of pinning going up to $63.5 \pm 0.1$ GPa for 25% pinned. The results show that 25% is likely unreasonably high for practical purposes but even the more realistic 7% run is significantly harder at $37.7 \pm 0.2$ GPa.
Chapter 1

Introduction

Modern cars are made of better, harder and tougher steels than they used to be. This move has had many benefits. Since everything can be made thinner, the result is lighter and more fuel efficient cars, which are also cheaper to produce. However, as the hardness of the steel used has increased, so the difference in hardness between the production tools and the material they are shaping has decreased. This has resulted in much greater mechanical wear of those tools. Since shaping tools are expensive and it seems likely that the problem will only get worse as still better steels are developed, there is considerable interest in discovering more about the precise mechanisms of mechanical wear of this type and how to reduce it.

There is already a considerable amount known on the topic, in particular thanks to early work by Bowden and Tabor on friction between both similar and dissimilar metals[1]. Archard built on that to describe mechanical wear by means of asperity interaction[2]. 'Asperity' is a specific term for the microscopic bumps on the surface of a material. A basic theoretical model for asperity interaction was set out by Challen and Oxley[3] but the finer details and experimental work are still ongoing. Asperities then, are an interesting avenue of study, however physical experiments are relatively expensive and when doing them it is not generally possible to track step-by-step exactly what is happening at each point of a test, especially at the atomic level. As such, most information has to be deduced from what can be seen of the end result. It would therefore be useful to be able to use computer simulations to model what is happening; they allow for such exact tracking and, in addition, are in principle cheaper.

One type of simulation which could be useful is that where every atom is individually modelled, this is known as Molecular Dynamics or MD. MD is one of the older simulation techniques[4] and allows one to track exactly what is happening to any atom at any point in time. However, due to the need to know all possible interaction potentials, it is at present in practice usually only possible to make simulations involving one or two elements. Steels by definition contain a minimum of two elements (iron and carbon) but all the steels of interest contain at least three or more. It is not possible, therefore, to simulate high hardness steels directly using MD but there may be ways to alter the hardness indirectly.

This train of thought led to the subject of this study: “Is it possible to alter the hardness of a Molecular Dynamics simulation by attaching a number of atoms to pinning points by means of springs?” Additionally, should the answer to that question prove to be yes there are further questions to be answered such as: “How realistic is this method of inducing hardness?” and “What mechanisms are involved and how similar are they to those that exist in reality?”

This was investigated by performing the same simple indentation test on a set of otherwise identical
body-centered cubic (BCC) iron simulations, varying only the presence and number of pinning points. Additionally, a smaller set without any pinning points was used to find the variability inherent in the simulations.

MD simulations of nano-indentation have been covered quite extensively, starting in 1990 by Landman et al. on a small nickel-gold simulation[5]. Iron is not as common as, for instance, copper for these tests but there are two studies by Lu et al.; one on the effects of different substrate crystallographic orientations[6] and another on the effects of different indenter shapes[7]. Neither of those involved pinned atoms in the substrate and nor do any other indentation simulations on any other elements. This then would be an entirely new technique, potentially of use not just in BCC iron simulations but in principle also for simulations involving any element and any crystal structure.

This report will begin with a chapter covering the methods used which also explains in short the theory behind them. Next comes a chapter with a detailed account of the results. After that there is a discussion of those results before the final chapter with the conclusions and suggestions for future study.
Chapter 2

Methods

2.1 Overview

This chapter begins with a summary of the tools used. Specifically, the hardware on which the simulations and the analysis thereof were run and the software configuration of those systems. Next, there is a short explanation of Molecular Dynamics simulations and of Camelion[8], the MD software used. After that, the settings of certain variables in Camelion of interest to these simulations are considered. The subsequent subsections (2.5 and 2.6) explain the way the indenters are made and the way the pinned atoms are assigned. Subsection 2.7 goes through an example run from start to finish. Then the analysis of the runs is explained in subsection 2.8, including the scripts used to obtain the graphs and images shown in chapter 3. The final subsection (2.9) is a short explanation of what could be expected in the way of results.

2.2 Tools

Two different systems were used during the simulations. All testing and the initial batch of runs were done using a Mac Pro running OSX and Camelion version 11.53, compiled with gfortran. The final set of runs were not performed on the Mac but on an Intel-based computer running 64bit Windows 7. As there is no version of Camelion for Windows a series of VMs (virtual machines) were used. The VM software used was Virtualbox 4.2 [9], each VM had 2 Gb of internal memory (RAM equivalent), one processor core and ran Ubuntu Linux 12.10 (sometimes referred to as 'Quantal Quetzal' [10]). These VMs were then used to run Camelion 11.53, again compiled with gfortran.

Using VMs is not a fast method for running simulations but it does allow for them to be run in the background on an entirely different operating system while the computer is used for other tasks. The VMs can be cloned to run multiple simulations in parallel, with the primary limitation being the RAM required. On this computer only two simulations could run in the background without significantly affecting other applications. In theory the VMs can be frozen and resumed at a later date or copied to another computer but these possibilities were not used in practice.
2.3 Molecular Dynamics and Camelion

Molecular Dynamics (MD) is a simulation method for the movement and properties of groups of particles. It works by numerical integration of the equations of motion for each of the particles. In this set of simulations those particles are individual atoms, but they can be larger clusters. Generally, as in this project, only Newtonian mechanics is considered:

\[ \vec{F} = m \cdot \vec{a} \]  \hspace{1cm} (2.1)

where \( F \) is the force acting on the particle, \( m \) its mass and \( a \) the resulting acceleration. The force is derived from an interaction potential, the one used in these simulations will be covered in more detail in a subsequent subsection. For this explanation a simple Lennard-Jones potential for the interaction between two atoms will be used instead:

\[ U(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]  \hspace{1cm} (2.2)

where \( U \) is the potential energy, \( r \) is the distance between the two atoms, \( \varepsilon \) is the depth of the potential well and \( \sigma \) is the distance at which the interaction potential can be set to zero. The force on atom 1 as a result of the interaction potential can be found as follows,

\[ \vec{F}_1 = -\nabla_1 U \]  \hspace{1cm} (2.3)

and for atom 2 analogously. The force is directed along the line between the two atoms. The Lennard-Jones potential is shown here for the interaction between two atoms, therefore this only provides the force on two atoms due to each other. For the net force acting on a single atom in a much larger atomic configuration it is necessary to calculate the force between each and every pair of atoms in the simulation. For small simulations with only a few tens of atoms this is still manageable, but the number of required calculations appears to increase quadratically as the number of atoms in the simulation increases. In practice, however, only a small number of atoms are close enough to need to be considered, thereby making the computational load scale linearly with the number of atoms.

There are several different iteration algorithms to determine the next set of positions and velocities as time progresses in the simulation. Camelion uses Velocity-Verlet[11], shown here:

\[ \vec{x}(t + \Delta t) = \vec{x}(t) + \vec{v}(t) \Delta t + \frac{1}{2} \vec{a}(t) (\Delta t)^2 \]  \hspace{1cm} (2.4)

\[ \vec{v}(t + \Delta t) = \vec{v}(t) + \frac{1}{2} \vec{a}(t) \Delta t + \frac{1}{2} \vec{a}(t + \Delta t) \Delta t \]  \hspace{1cm} (2.5)

where \( t \) is the time, \( \Delta t \) is the time-step and \( \vec{x} \) and \( \vec{v} \) are respectively three dimensional vectors for position and velocity, the acceleration \( \vec{a} \) is what was calculated from the interaction potential by way of the force.

\[ \vec{a} = \frac{\vec{F}}{m} = \frac{-\nabla U}{m} \]  \hspace{1cm} (2.6)

In Camelion the size of the time-step is re-calculated every step to ensure that no atom moves by more
than a set distance $\Delta r_{\text{max}}$, currently set to 2 pm:

$$(\Delta r_{\text{max}})^2 < (\vec{v} \cdot \vec{v}) (\Delta t)^2 + (\vec{a} \cdot \vec{v}) (\Delta t)^3 + \frac{1}{4} (\vec{a} \cdot \vec{a}) (\Delta t)^4$$ \hspace{1cm} (2.7)

In these simulations, as in many cases, it is useful to run at a fixed temperature. To set the temperature of the simulation Camelion uses a Berendsen thermostat\cite{12}. At each time-step the temperature of the system (or that of a chosen subset) is calculated from the atomic velocities by taking the average of

$$T = \frac{m}{3k} (\vec{v} \cdot \vec{v})$$ \hspace{1cm} (2.8)

where $T$ is the temperature and $k$ is the Boltzmann constant. When the result deviates from the set temperature the velocities are rescaled.

In order to simulate a bulk crystal periodic boundaries are used, where the crystal is modelled as being surrounded by identical copies of itself which follow the exact same dynamics. This results in a crystal of infinite size in all directions. For other situations, it is also possible to have periodic boundaries in only some directions or to have atoms that cross an imaginary boundary disappear from the simulation.

This project uses the pinning functionality in Camelion. A pinned atom is not itself fixed in place, rather it is attached to an anchor-point by means of a spring. The anchor-point is fixed in place, or as in the case of the indenter, moved. The pinned atoms are thus not moved directly but are, in addition to the forces from other atoms, affected by the spring-force

$$\vec{F} = -c \cdot \vec{r}$$ \hspace{1cm} (2.9)

where $c$ is the spring-constant and $\vec{r}$ is the vector between the atom and its anchor-point. The spring-constant is set by the user in the $goion$ input file, which will be covered in more detail later.

For practical reasons Camelion works internally with the Boltzmann constant set to 1 rather than $1.38 \cdot 10^{-23} \text{JK}^{-1}$, this works because all related quantities such as temperature are also rescaled. Table 2.1 shows the units used. It is necessary to apply these conversions to both input and output.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>2.684e-10 m</td>
</tr>
<tr>
<td>Mass</td>
<td>9.75e-26 kg</td>
</tr>
<tr>
<td>Temperature</td>
<td>1012 K</td>
</tr>
<tr>
<td>Time</td>
<td>0.709 ps</td>
</tr>
<tr>
<td>Velocity</td>
<td>379 m/s</td>
</tr>
<tr>
<td>Force</td>
<td>5.21e-11 N</td>
</tr>
<tr>
<td>Force-constant</td>
<td>0.194 N/m</td>
</tr>
<tr>
<td>Energy</td>
<td>0.0872 eV</td>
</tr>
</tbody>
</table>

Table 2.1: Conversion factors for the units used by Camelion. The first four are the base units. All others are derived from them.

**Camelion File-types**

Here follows a short explanation of the Camelion input and output file-types referenced throughout this report.
Cn-file: configuration file, cn-files are both an input and an output file-type. They contain the number of atoms, the size of the simulation box and the simulation time as well as the positions, velocities, type (in case of multiple atom types), potential energy and an id-number for each of the atoms in the simulation.

Bt-file: bottom file, the bt-file is only an input file. It contains the size of the simulation box as well as the anchor-point positions, id-number and type of the pinned atoms. anchor-points of type 3 are pinned in place while those of type -3 will move along the path listed in the pp-file.

Pp-file: pulling path file, the pp-file is an input file. It consists of a list of times and x,y,z positions relative to the starting situation. The -3 anchor-points follow (as a rigid lattice of points) the path that linearly interpolates the x,y,z positions in the file.

Goion-file: go ion file, the goion-file is the primary settings file for any run. It contains many options and only the ones most relevant to this report will be listed here. It is where the potential needs to be listed, as well as the temperature and pressure with any gradients in either. The goion-file also keeps track of whether to use pinning points and if so what the spring constant (named force-constant) is and whether the pinning points are to be moved according to the path in the pf-file.

Pf-file: pulling force file, an output file with a list of times and of the anchor-point forces working in each of the three directions on all atoms of type 3 and those working on atoms of type -3.

2.4 Settings

The potential used was an Embedded Atom Model[13] (EAM) potential. EAM potentials are of the form

\[ E_i = F_\alpha \left( \sum_j \rho_\beta (r_{ij}) \right) + \frac{1}{2} \sum_j \phi_\alpha_\beta (r_{ij}) \]  

(2.10)

where \( E_i \) is the potential energy of atom \( i \), \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( \phi_\alpha_\beta \) is a pair-wise potential function, \( \rho_\beta \) is the contribution to the electron charge density from atom \( j \) of type \( \beta \) at the location of atom \( i \) of type \( \alpha \), and \( F_\alpha \) is an embedding function that represents the energy required to place atom \( i \) into the electron cloud. The specific variant used for these simulations was the Zhou-Wadley Fe-Co potential [14], which, as the name implies, can be used to simulate iron (Fe), cobalt (Co) or Fe-Co alloys. The functions \( F_\alpha \), \( \rho_\beta \) and \( \phi_\alpha_\beta \) can be found in [14].

The (free) compiler used to compile Camelion on the two systems has limits on the amount of memory that may be used. This indirectly affects the maximum number of atoms in the simulation. As such, the maximum number of atoms for each of the runs was no more than 62,000.

The substrate is initiated with sides of 10 nm, which due to the way the crystal builder works, the crystal orientation (111) and the slight relaxation, ends up being approximately 9.7 nm by 9.9 nm. The height of the substrate is variable depending on the number of atoms needed for the indenter. For conical indenters the height is 4.5 nm and for Berkovich it is 4 nm.

For the springs, the Camelion parameter "force-constant" was set to the somewhat arbitrary value of 999, corresponding to a spring-constant of 194 Nm\(^{-1}\). For this experiment this is equivalent to an elastic constant of 235 GPa, which is higher but of the same order as that of iron (211 GPa).
2.5 Indenters

The indenters were created by first running a simulation of a block of the desired atoms, periodic in $x$, $y$ and $z$, to simulate a bulk crystal under standard pressure and temperature until relaxation. After this any atoms located outside the desired indenter shape were discarded.

In the first stages a conical shape was used, due to its mathematical simplicity.

$$x^2 + y^2 \leq z^2 \quad (2.11)$$

Where $x$, $y$ and $z$ are the coordinates of any individual atom. This particular variant has a slope of 45 degrees, for an arbitrary angle this requires modifying by $z^2 \Rightarrow z^2 \tan(\theta)$.

This simple indenter was used for most runs but tests were also run with two other types. First a four-sided pyramid shape:

$$|x| \leq z \geq |y| \quad (2.12)$$

which, depending on the angle of the crystal lattice, can have some benefits regarding the match between the intended indenter shape and the actual placement of the atoms.

Finally a complex three sided Berkovich indenter was tested:

$$y \leq z \cdot \tan(65) - \frac{|x|}{\tan(30)} \quad (2.13)$$

$$y \geq -z \cdot \tan(65) \cdot \cos(60) \quad (2.14)$$

which is the indenter type used in many physical experiments. However, the properties that make it a much used indenter in real-world testing also make it impractical for simulations. The triangular shape is not a significant issue but the indenter also has a very obtuse point. This means that the width of the indented area increases rapidly as a function of the penetration depth, something which is not an issue with large bulk samples but is a major problem for simulations which are severely limited in the total number of atoms used.

Table 2.2 shows all the runs covered in this report including the percentage of substrate atoms pinned and both the shape of the indenter and its velocity.
2.6 Pinning

In this project, the question was whether it is possible to influence the hardness of a simulated block of iron by pinning a certain percentage of the iron atoms in the simulation. This could be done in a variety of ways.

It is possible to pin a line, plane or (extra) half-plane of atoms. These pinned atoms would be somewhat analogous to dislocations, a known cause of hardness in materials[15]. However dislocations already occur in simulations so this does not add anything new.

Simply pinning a block would somewhat simulate nanoscale precipitates but it could be assumed that the exact placement of the block relative to the indented area would strongly affect results.

Finally, the most interesting option is to pin a percentage of the atoms in the substrate at random. The hardness is measured at different pinning percentages while the rest of the system remains the same. The situation somewhat resembles foreign atom types in solution hardening, which is a hardening mechanism present in, for example, brass. However it is only somewhat similar since the potential used for those pinned atoms is still that of iron and they are permanently elastically tied to their anchor-points.

To get a percentage of atoms pinned a random number generator is used. For this set of simulations it was the awk RAND() function, a built-in (pseudo)random number generator.

2.7 Simulations

Each simulation is run from a script for ease of repetition. An example is shown in appendix A.1.

The simulation starts by creating the crystal that will form the indenter. It then runs this crystal with periodic boundaries at “room temperature” (300 K) for a preset period of time, assumed to be sufficiently long for the crystal to relax to steady-state. Then, as explained in subsection 2.5, the indenter is made by discarding atoms outside the desired shape.
The number of atoms available for the substrate is then determined by subtracting the number of atoms in the indenter from the maximum allowable - in this case 62,000 as explained in subsection 2.4. The substrate is created with the same width (in both $x$- and $y$-directions) as the block from which the indenter is cut. Depending on the height of the indenter-block, which is in turn dependent on the intended indentation depth and the shape of the chosen indenter, the indenter usually ends up much smaller, even at its widest point. The height of the substrate is calculated based on the number of full $z$-direction planes possible with the given number of atoms. There is no check that the substrate is large enough to perform the test in any of the three directions, this is left to the user.

After relaxation of the substrate under the same conditions and for the same amount of time as the indenter-block the two parts are put together with a pre-set spacing, here approximately 0.25 nm.

The following step is to create the *pp-file*, which indicates how the pinned atoms of type -3 (here the indenter atoms) will move. The *pp-file* contains only times and $x$, $y$ and $z$ positions relative to the starting point. The script generates a *pp-file* with short pauses of 0.7 ps every 0.25 distance-steps, or approximately 0.06 nm. These pauses are found in other MD simulation based studies\[16, 17\], however since only the anchor-points were moved and since the indenter velocity used was relatively low they are probably unnecessary here.

The final step before the simulation of the indentation is to create the *bt-file* indicating which atoms are to be pinned and what type they are. The first group is the indenter atoms, all of which are pinned as type -3 indicating that their pinning points will move as dictated by the *pp-file* described above. All the remaining pinning points are of type 3 and therefore will not move according to the path in the *pp-file* but will remain in the starting positions throughout the run. To prevent the indenter from pushing the substrate away the bottom 0.75 nm of the substrate crystal are pinned. The same is done for the sides to prevent bulging or turning the simulation into a multi-indenter one (as would be the case for only periodic boundaries), all boundaries are also set to be non-periodic. As explained in subsection 2.6, the remaining bulk of the substrate has a percentage of its atoms pinned. This pinned percentage is the only variable for different runs in the same set.

2.8 Analysis

Time-series

The time-series are drawn using the pgfplots package of \LaTeX. To make the slices and make it possible for pgfplots to colour the different atom-types appropriately, the R-script “TimeSlices” shown in appendix A.3 is used. The script first reads in the *cn-file* and associated *bt-file* for the required slice. Then it steps through the file. If an atom is inside the defined slice it checks what type (indenter, substrate-pinned, substrate-unpinned) the atom is in the *bt-file*. Finally it outputs one file for each atom type with the coordinates for all the atoms. For convenience, it is currently set to make all timesteps for one run at once. At this point there is no conversion between Camelion’s units and their real-world counterparts as only the relative positions are of interest. These three files are plotted using the pgfplots \LaTeX package to create the final image.
Force-time, Force-depth, Hardness-depth

The data for these three plots is all produced simultaneously by the R-script “FTFDHDplots” shown in appendix A.4. This script generates the three files that pgfplots uses to make the actual plots shown in the report.

It starts by reading in the data from the *pf-file* and *pp-file* that will be used to make the plots. The *pf-file* lists the anchor-point forces acting on each set of atoms (the two groups being the stationary pinned atoms and the pinned atoms that move as dictated by the *pp-file*) at frequent intervals during the simulation. It consists of seven columns, the first is the time, the second to fourth are the x, y, z forces on the moving atoms and the fifth through seventh are the x, y, z forces on the stationary atoms. The *pp-file* is one of the input files described in section 2.3 and lists how the indenter moves in time. The forces, times and distances in both files are in Camelion’s internal units. The conversion factors for those three are $5.21 \times 10^{-11}$ to convert force to N, 0.709 for time to ps and 0.2684 for distance to nm.

For the force-time plot file the script converts the force (column 4, the force on the indenter in the z direction) to Newtons and the time to picoseconds. Then it does block averages over every 200 timesteps to reduce the number of datapoints to a more practical number. The result is then written to a file.

For the depth-force plot it starts by taking the *pp-file* to find which times correspond to each depth. The corresponding forces are found from the pf-data and again the numbers are averaged and converted before being written to the depth-force plot file.

The final plot in the set, with the calculated hardness as a function of depth starts with the data from the previous depth-force dataset. The hardness can be calculated from the force through

$$H = \frac{F}{A}$$

(2.15)

where A is the nominal value of the projected area of the indenter. For the different indenters used these areas are as follows:

The most used indenter shape was the cone with a 45 degree angle where the area is

$$A = \pi d^2$$

(2.16)

with $d$ the indentation depth.

For the Berkovich indenter (used in a few runs)

$$A = \frac{3\sqrt{3}}{8} \cdot d^2$$

(2.17)

and for the four-sided pyramid (used only in test runs)

$$A = (2d)^2$$

(2.18)

The final hardness value for each run is defined as the mean for all datapoints where the depth is greater than 1.5 nm.
2.9 Expectations

This leads us to consider what might be expected in the way of results. The proposed hardening method of pinning a percentage of atoms bears the closest resemblance to solid-solution hardening. For steels solid-solution hardening was studied extensively in the early to mid-1900s by, amongst others, Austin. A general overview of the results of those studies are shown in figure 2.1. This shows that the hardness increases vary by between 10% and 400%, depending on the type of atom, over the range from 0% of atoms in solid solution to 5% in solid solution. The progression seems quite variable as well with manganese (Mn) appearing almost linear between 1% and 5% where the rest are closer to either a second or higher order polynomial or to an exponential function.

Since there are such different responses for different elements in ferrite, the curve describing the relationship between the percentage of pinned atoms and the hardness need not have a specific shape for for the simulation results to be comparable to real materials. Primarily then, there should be an increase in hardness for each increase in pinning percentage with the exact nature of that increase being of lesser concern.

![Figure 2.1: General overview of the change in hardness for various alloying elements in ferrite. It uses the Vickers hardness scale which can be multiplied by 9 to convert to MPa, so the values range, roughly speaking, from 550 MPa to 2 GPa.][18]
Chapter 3

Results

This chapter will begin with a short overview, followed by summaries of each of the runs with the results for each individual run. The runs can be divided into three sets, the first ten are with a conical indenter with a varying percentage of pinned atoms, after that there are two with a Berkovich indenter and finally a set of five under identical conditions to test the reproducibility. These results include a time-series showing the progress of the indentation, two three-dimensional figures showing the views at maximum indentation depth and after withdrawal, a plot with the force measured at each point in time, the same but with the time converted to the depth of the indenter and, finally, the calculated hardness against the depth. After the summaries there is a section with some multi-run comparisons and the aggregated results.

3.1 Overview of the simulations

This section covers the results from the simulations. Each run produces a series of \textit{cn-files} (configuration) which contain, among other things, the positions of each atom in the simulation. The \textit{cn-files} are made every 3.5 ps. Corresponding to each set of \textit{cn-files} there is a single \textit{pf-file} (pulling force), indicating the force acting on each group of atoms in all three directions over time.

There are two three-dimensional images to visualize the indentation, one while the indenter is at its deepest and one after the indentation is complete. Both images are created using OVITO\cite{19}, they have the atoms coloured by atom-type (pinned-indentener, pinned-substrate, unpinned) and the unpinned atoms are additionally coloured by height. The required conversion script (Camelion to OVITO) can be found in appendix A.5 and is a slightly modified version of the TimeSlices script explained in detail in section 2.8. The second image shows all atoms, but the first only shows those atoms not in a body-centered cubic (BCC) configuration (and cuts off the bottom and sides) to visualize what happens inside the substrate during indentation and show the presence or absence of dislocations.

In addition to the two three-dimensional images, this report shows a slice a few atomic layers thick at six time points throughout the indentation. The procedure used is explained in more detail in section 2.8, but it involves using an R-script 'TimeSlices' (see Appendix A.3) to produce files which are then used by the pgfplots \LaTeX package to draw the graphics.

A different R-script 'FTFDHD' (see Appendix A.4) is used to produce the data for the other three plots (time-force, depth-force and depth-hardness). The procedure is as explained in section 2.8, involving
unit conversion, averaging due to the number of data-points and using the **pp-file** (pulling path) to calculate the projected area of the indenter and thereby the hardness.

*To avoid excessive duplication of comments, only the first (0% pinned) run is covered in detail. For the remaining runs the comments relate only to differences and any unusual features.*

### 3.2 Conic indenter with 0% points pinned

This run has zero percent pinning points, a material equivalent to pure iron. However, as explained in chapter 2.1 this does not mean that no points are pinned. A few layers are pinned at the bottom of the sample to prevent the whole substrate moving down. Similarly the sides are pinned to simulate the rest of the material as if it were infinitely undeformable. Simply using periodic boundaries would simulate a multi-indenter test rather than the single one intended in this simulation.

The results for this run are shown in figures 3.1, 3.2 and 3.3.

Figure 3.2 is a time-series showing the progression of the simulation, using a slice through the middle of the crystal 0.3 nm wide, which means it will show only one or two atomic layers. The first frame is before the indentation begins, the second halfway through the indentation and the third is at maximum depth which corresponds to the three-dimensional view shown in figure 3.1a. The second line shows the withdrawal, with the first frame at one third, the second frame at two thirds and the final frame showing the end state where the indenter is back at its original position, corresponding to the three-dimensional view shown in 3.1b.

As can be seen the indentation has a dramatic effect on the substrate with the atoms in the area where the indentation takes place mostly being displaced to greater depth during the indentation, while a smaller number form a layer on the side of the indenter. The displacement causes dislocations, visible in figure 3.1a as the loops of non-BCC atoms. The dislocations extend across most of the width and depth of the substrate. As the indenter withdraws the atoms that were displaced deeper or to the side reform the original crystal structure, although some of those on the sides of the indenter remain there, increasing the size of the indenter and leaving a hole in the substrate. The dislocations disappear again in their entirety indicating that no work-hardening has taken place. There does not appear to be any noteworthy pile-up of atoms on the substrate around the site of the indentation, however there are three tendrils still extending from within the indentation site to the indenter.

The top plot in figure 3.3 shows the force on the indenter atoms as a function of time. Before any contact is made with the substrate the measured force oscillates around zero rather than being constant. This is due to the temperature being above absolute zero resulting in some small movement of the atoms around their anchor-points. This registers as a small randomly directed force which averages zero over time, but need not be zero at any individual point in time. The force measured during indentation is, however, clearly orders of magnitude higher.

During the indentation the force is positive but there is also a smaller negative force during removal. This is expected and due to the atoms being in a lower energy state while in contact with other Fe-atoms as opposed to vacuum, in other words, the indenter sticks to the substrate.

To make the different stages clearer, the middle plot of 3.3 is of the same dataset as the top plot of 3.3 but the time-scale has been converted to depth and some additional averaging done over the
Figure 3.1: 3D views of 0% run 901. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

(a) Initial state, depth is -0.25 nm.
(b) Halfway through indentation, depth is 0.8 nm.
(c) Maximum depth, 1.6 nm.
(d) One third, depth is 1 nm.
(e) Two thirds, depth is 0.5 nm.
(f) Final state, depth is -0.25 nm.

Figure 3.2: Time-series of run 901 with 0% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
Figure 3.3: Time-force (top), depth-force (middle) and depth-hardness (bottom) plots for run 901 with 0% pinning of the bulk.

data-points. In this form it is easier to see that the force builds during the indentation but does not immediately decrease to zero or negative values upon the start of the withdrawal. This is explained by the atoms shown in figures 3.2 and 3.1a to have been displaced to greater depth, these will continue to exert an upwards (positive) force on the indenter atoms until they can reform in a less disturbed structure.

The final plot of the set shown in figure 3.3 gives the hardness as a function of depth. At very small indentation depth the number is highly uncertain, due to the uncertainty in the area of the indenter at those depths as that area consists of only a few atoms and to the very small magnitude of the force. Beyond 0.5 nm the uncertainty rapidly decreases and the values for the hardness stabilize.

The final hardness value is taken as the average for the points at depths between 1.5 nm and 1.6 nm, which for 0% pinning is 21.6 ± 0.2 GPa. The error given here is that for a single run, however it will be shown later in section 3.13 that the variation between two simulations that use the exact same settings is roughly an order of magnitude larger.

3.3 Conic indenter with 1% of points pinned

For run 902 where 1% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.4, 3.5 and 3.6.

The 3D-views and time-series shown in figures 3.4 and 3.5, respectively, have a few obvious differences when compared to those of the previous run. First there are the pinned bulk atoms in red. They do not
Figure 3.4: 3D views of 1% run 902. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

(a) Initial state, depth is -0.25 nm.
(b) Halfway through indentation, depth is 0.8 nm.
(c) Maximum depth, 1.6 nm.
(d) One third, depth is 1 nm.
(e) Two thirds, depth is 0.5 nm.
(f) Final state, depth is -0.25 nm.

Figure 3.5: Time-series of run 902 with 1% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
move from their positions throughout the indentation and withdrawal. Secondly, the displaced atoms did not move as much or, at least, did not cause as wide ranging dislocations. There are still visible dislocation loops, of which one can be seen on the right hand side of figure 3.4, but they are contained in a small area near the indenter. This is the first indication that dislocation motion is reduced by atom pinning.

After the indenter is withdrawn the hole left is slightly deeper but less wide than it was for 0% pinning but the surface is rougher. There are no tendrils between the indenter and the substrate.

The time-force plot in figure 3.6 is similar to that of figure 3.3, though it appears to be smoother and has a sharper peak. The maximum is higher but the minimum is barely lower. As could be expected from the similarities in the time-force plot the depth-force plots are also very similar. The higher maximum is clearer as is the slight increase in smoothness. The hardness plot is almost identical in structure, with a random pattern of points until approximately 0.5 nm, after which it varies comparatively little but the final value is higher.

The final hardness value for 1% pinning run 902 is $25.0 \pm 0.2$ GPa.

### 3.4 Conic indenter with 2% of points pinned

For run 904 where 2% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.7, 3.8 and 3.9.

Figure 3.8 has several noteworthy features. This is the first time-series with pile-up visible at the
(a) 3D view at maximum depth of indentation. Only atoms not in a BCC-configuration are shown.
(b) 3D view after indentation.

Figure 3.7: 3D views of 2% run 904. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

(a) Initial state, depth is -0.25 nm.
(b) Halfway through indentation, depth is .8 nm
(c) Maximum depth, 1.6 nm
(d) One third, depth is 1 nm
(e) Two thirds, depth is 0.5 nm.
(f) Final state, depth is -0.25

Figure 3.8: Time-series of run 904 with 2% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
The pile-up on the right hand side remains even after withdrawal, with a corresponding gap in atoms covering the indenter. This is not visible in the 3D views as they are from another angle. The 3D views show that like in the previous two runs there is a clear dislocation loop at maximum indentation with several pinned atoms on the outside of that loop. As with the 1% run the total area covered by the dislocations is considerably smaller than it was for the 0% run. In the post-indentation 3D view there are again, like in the 0% run, tendrils between the indenter and the substrate.

This is also the first run where one of the pinning points falls inside the indented area, visible as one red atom inside the green indenter in figure 3.8c. In this case is is near the edge of the indented area and the crystal reforms to include it. Figure 3.7b shows that there was a second one, again close enough to the edge to be included during the reforming of the crystal.

For the force-time plot shown at the top of figure 3.9 the maximum has again increased noticeably compared to runs 901 and 902 without a corresponding change in the minimum. While all the force-time and force-depth plots show peaks and drops, these time-force and depth-force plots are the first to show a plateau. Between 1 nm and 1.2 nm there is no change in the force required to move the indenter, though it does start increasing again at 1.2 nm. The hardness plot at the bottom of figure 3.9 is somewhat different to the preceding runs in that the value does not settle until 0.6 nm, which is deeper than 901 and 902 where it was 0.5 nm. Even after 0.6 nm it shows considerably more change than do runs 901 and 902 with first an increase until a depth of 1 nm is reached and then some oscillations.

The final hardness value for 2% pinning run 904 is $28.2 \pm 0.2$ GPa.
Figure 3.10: 3D views of 5% run 905. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

3.5 Conic indenter with 5% of points pinned

For run 905 where 5% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.10, 3.11 and 3.12. As stated in the introduction to this section the plots are the same for all sections and the 0% run summary has some additional general comments which are not repeated here.

Like run 904, shown in figure 3.8, the 5% time-series shown in figure 3.11 has anchored substrate atoms inside the indented area. Unlike run 904, in this run one of them is too far removed from the sides for the crystal to reform around it leading to it being left hanging in the vacuum after withdrawal, this is also visible, though not as clearly, in figure 3.10b. This is a side effect of the pinning method and would obviously not be expected to happen in a real material. Run 905 is the first run that has no dislocation loops at any point in the indentation and as can be seen in figure 3.10a, the lattice distortions are localized next to the indented area. The final situation in figure 3.11f shows a single atom chain spike due to the placement of pinned atoms. While there is pile-up during indentation just as there was for the 2% run, in this case there is none left after withdrawal in the 2D view. In 3D there is some disturbance of the surface as in all previous runs, but there are no tendrils as there were for runs 901 and 904.

As during run 904, the top and middle time-force and depth-force plots for run 905 in figure 3.12 show a plateau between roughly 200 ps and 240 ps or 1 nm and 1.2 nm. The minimum remains unchanged while the maximum has increased by roughly 50% since run 901. The hardness plot at the bottom of figure 3.12 is similar to the one in figure 3.9, with a steady increase between 0.6 nm and 1 nm. Between 1 nm and 1.6 nm it oscillates with a slight overall downward trend.

The final hardness value for 5% pinning run 905 is $34.6 \pm 0.1$ GPa.
Figure 3.11: Time-series of run 905 with 5% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
Figure 3.12: Time-force (top), depth-force (middle) and depth-hardness (bottom) plots for run 905 with 5% pinning of the bulk.

3.6 Conic indenter with 7% of points pinned

For run 906 where 7% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.13, 3.14 and 3.15.

The time-series shown in figure 3.14 has two pinning points inside the indentation site, with several more visible in figure 3.13b. As with run 905 not all are included when the crystal reforms. Unlike run 905 there are no spikes or pits due to the placement of pinning points.

Figure 3.14d shows a gap as having formed between indenter and substrate relatively early compared to other runs, specifically, on the left hand side.

As can be seen in figure 3.13a, a dislocation loop does again form unlike in run 905. The depth and width of the distortions is also slightly greater than it was for the last run, though it is smaller than for runs 901, 902 and 904.

As seen in the time-force plot at the top of figure 3.15 and more clearly in the depth-force plot in the middle, run 906 does not have a plateau between 1 nm and 1.2 nm where runs 905 and 904 did. There is instead a shorter and less smooth plateau between 1.4 nm and 1.5 nm.

Unlike any preceding run, after the values start stabilizing at 0.6 nm there is a slow but steady increase until the run finishes at 1.6 nm.

The final hardness value for 7% pinning run 906 is $37.7 \pm 0.2$ GPa.
Figure 3.13: 3D views of 7% run 906. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

Figure 3.14: Time-series of run 906 with 7% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
3.7 Conic indenter with 10% of points pinned

For run 803 where 10% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.16, 3.17 and 3.18.

Run 803 comes from an earlier short set of test runs, the only real difference with the runs in the 900 range is that 803 is missing the "cn-file" for the final time-step. Instead the time-series and 3D view use an earlier one where the indenter is at the height of the original surface. The atoms are also in slightly different positions resulting in the slices containing less atoms.

As with all prior time-series aside from the 2% one, the series shown in figure 3.17 has noticeable pile-up at the maximum indentation depth but none (in this plane) after withdrawal. The 3D view in figure 3.16b shows that this is not just an artefact, there is indeed only a crater left after indentation, without any pile-up. All the excess has been picked up by the indenter.

There are a considerable number of pinning points inside the indentation area, the positioning of which in this case has resulted in reforming of the lattice in such a way as to include them leading to the two small (red-tipped) spikes in the final frame of the 2D series.

As in 5% run 905, figure 3.16a shows that no dislocation loops have formed and that the distortions are localised near the indented area.

As shown in the top and middle time-force and depth-force plots of figure 3.18, while runs 904-906 all had clear plateaus, run 803 did not. New to all runs is the jaggedness, particularly visible in the time-force plot, during withdrawal. This is likely to be related to the number of pinned points inside
(a) 3D view at maximum depth of indentation. Only atoms not in a BCC-configuration are shown.

(b) 3D view after indentation.

Figure 3.16: 3D views of 10% run 803. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

(a) Initial state, depth is -0.25 nm.
(b) Halfway through indentation, depth is .8 nm
(c) Maximum depth, 1.6 nm
(d) One third, depth is 1 nm
(e) Two thirds, depth is 0.5 nm.
(f) Final state, depth is 0

Figure 3.17: Time-series of run 803 with 10% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
Figure 3.18: Time-force (top), depth-force (middle) and depth-hardness (bottom) plots for run 803 with 10% pinning of the bulk.

3.8 Conic indenter with 15% of points pinned

For run 907 where 15% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.19, 3.20, 3.21 and 3.22.

Figure 3.19a shows no dislocation loops, but instead a large number of pinned atoms on the edge of the distorted area as could be expected with the high pinning percentage. For the same reason, the time-series for run 907 shown in figure 3.20 shows at least half a dozen inside the indentation area. Some remain in the vacuum after withdrawal, what is new with this run is that a non-pinned atom has joined them, attached to one or more pinned atoms outside the slice. Figure 3.19b shows that the number of pinned points it now high enough that there are chains of pinned atoms left in the vacuum after withdrawal.

This run is the first where there is disorder visible after withdrawal. In figure 3.20f, in the area directly below the indentation area which is surrounded by pinned points but contains none, the atoms are slightly irregularly placed. This was not the case before the indentation as seen in figure 3.20a. To demonstrate there are two extra 3D views in figure 3.21 showing the stable distorted clump. The atoms
(a) 3D view at maximum depth of indentation. Only atoms not in a BCC-configuration are shown.

(b) 3D view after indentation.

Figure 3.19: 3D views of 15% run 907. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

(a) Initial state, depth is -0.25 nm.
(b) Halfway through indentation, depth is .8 nm
(c) Maximum depth, 1.6 nm
(d) One third, depth is 1 nm
(e) Two thirds, depth is 0.5 nm.
(f) Final state, depth is -0.25

Figure 3.20: Time-series of run 907 with 15% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
are not identified as being in any particular structure such as BCC, FCC (Face-Centered Cubic) or HCP (Hexagonal Close Packed).

The time-force plot for run 907 shown at the top of figure 3.22 has many small jumps in force during the indentation phase giving it a very jagged appearance. The withdrawal is also less smooth and has a somewhat different shape to the early runs. Like in several other runs there is a plateau visible in both top and middle plots. Once again it is between approximately 1 nm and 1.2 nm, though in the time-force plot (200 ps to 250 ps) it is clear that the plateau is not entirely flat but has several small jumps in force that cancel out with the averaging.

As with the preceding few runs, there is a steady upwards trend in the hardness plot at the bottom of figure 3.22. However this run has larger oscillations than those did, with differences of up to 20 GPa in the space of 0.2 nm.

The final hardness value for 15% pinning run 907 is $52.3 \pm 0.2$ GPa.
3.9 Conic indenter with 20% of points pinned

For run 908 where 20% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.23, 3.24 and 3.25.

There are no features in figures 3.23 and 3.24 not seen in runs with a lower proportion of pinned atoms. As with all the higher pinning percentages there are no dislocation loops visible in figure 3.23a.

None of the many pinned atoms in the indented area are left hanging in vacuum in the slice, due to a line being pinned. In the 3D view in figure 3.23b it is clear that in other planes there are many left hanging. There is considerable distortion during indentation but, unlike run 907, after withdrawal the distortion is no longer evident.

The coverage of the indenter by atoms from the substrate is somewhat less than in earlier runs with large parts of the indenter remaining uncovered as seen in figure 3.23b.

Neither the time-force plot, nor the depth-force plot shown in figure 3.25 shows a plateau. The most unusual feature of this set is the withdrawal where the force is almost reduced to zero on two separate occasions before again increasing to more negative values.

The hardness plot shown at bottom of figure 3.25 is also somewhat different from other runs in that there is a steep rise between 0.6 nm and 0.8 nm. After that there is still a slight upwards trend but without the large oscillations seen in run 907.

The final hardness value for 20% pinning run 908 is $59.8 \pm 0.2$ GPa.
(a) 3D view at maximum depth of indentation. Only atoms not in a BCC-configuration are shown.
(b) 3D view after indentation.

Figure 3.23: 3D views of 20% run 909. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

(a) Initial state, depth is -0.25 nm.
(b) Halfway through indentation, depth is 0.8 nm
(c) Maximum depth, 1.6 nm
(d) One third, depth is 1 nm
(e) Two thirds, depth is 0.5 nm.
(f) Final state, depth is -0.25 nm.

Figure 3.24: Time-series of run 908 with 20% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
For run 909 where 25% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.26, 3.27 and 3.28.

The time-series for the run with the highest practical proportion of points pinned is shown in figure 3.27. Although there are a significant number of pinned atoms inside the indented area the indenter itself does not appear distorted, which could have been an issue for determining the projected area.

As seen in figure 3.26a there are no dislocation loops and the distorted area is the smallest of any run. The coverage of the indenter in figure 3.26b is similar to the 20% run shown in figure 3.23b, with the tip of the indenter free of spare atoms.

This run has no extended plateaus visible in either of the force-plots (top and middle plots of figure 3.28). Like the 20% run it does however have a very different pattern on withdrawal than the low pinning point runs with several returns to (near) zero net force.

The hardness plot shown at the bottom of figure 3.28 has a very steep rise from only 20 GPa at 0.6 nm to over three times that by 1.6 nm.

The final hardness value for 25% pinning run 909 is 63.5 ± 0.1 GPa.
Figure 3.26: 3D views of 25% run 909. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

Figure 3.27: Time-series of run 909 with 25% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
Figure 3.28: Time-force (top), depth-force (middle) and depth-hardness (bottom) plots for run 909 with 25\% pinning of the bulk.

3.11 Conic indenter with 100\% of points pinned

For run 911 where 100\% of atoms in the substrate were pinned, not counting those pinned to fix the bottom and sides, the results are shown in figures 3.29, 3.30 and 3.31. This is not a pinning percentage that would ever be used, however it is interesting to see what exactly happens in such an extreme case. Not quite 100\% are pinned as a partial layer between the ones that are pinned on the substrate and the bulk remain unpinned as well as a thin layer on the surface.

Both the time-series in figure 3.30 and the 3D view in figure 3.29a show what might be expected from prior runs which is that the distortion is limited to only one or two atom-layers beyond the indented area. As can be seen in figure 3.30c the pinned atoms in the indented area and those of the indenter occupy the same area in a severely distorted lattice. After the indenter is withdrawn the pinned atoms all end up back in their original positions. The unpinned top layer over the indented area has ended up divided between the indenter, though as with the 20\% and 25\% runs the tip is uncovered, and there is some pile-up around the sides.

As would be expected for such a high pinning percentage the force-plots, as shown at the top and middle of figure 3.31, have a sharp peak with a very high maximum required force. The oscillations seen in the (top) time-force plot during withdrawal are likely caused by the two sets of pinned atoms moving past each other.

The spike in hardness at a depth of half a nanometre followed by a dip and then a steady upwards trend as seen in several of the later runs is even clearer in figure 3.31 (the bottom plot). The hardness
Figure 3.29: 3D views of 100% run 911. Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

(a) Initial state, depth is -0.25 nm.  
(b) Halfway through indentation, depth is .8 nm  
(c) Maximum depth, 1.6 nm  
(d) One third, depth is 1 nm  
(e) Two thirds, depth is 0.5 nm.  
(f) Final state, depth is -0.25

Figure 3.30: Time-series of run 911 with 100% pinning of the bulk. Each image shows all atoms present at that time-step in the middle 0.3 nm. Unpinned atoms are blue, pinned atoms in the substrate are red and the indenter is green.
measured in this final run is roughly an order of magnitude higher than it was for the first runs without pinned atoms.

The final hardness value for 100% pinning run 911 is $200.2 \pm 0.2$ GPa.

3.12 Berkovich indenter

The Berkovich indenter was tried as it is the most commonly used indenter shape for experiments. Since the results indicated this is not a practical configuration for simulations of this size only two runs were completed: 1% pinning run 501 and 5% pinning run 502. The results for the two runs are shown in figures 3.32 and 3.33.

As can be seen in figure 3.32 the indenter is much larger than the conical indenter, which leads to much more distortion of the lattice during indentation. There are more dislocation loops and they run through the entirety of the unpinned part of the substrate, including into the corners. The increased pinning percentage in run 502 (figure 3.32b) over run 501 (figure 3.32a) results in less visible dislocation loops, but more distortion overall.

It is also clear that the indenter is so obtuse that the edges of the indenter move through the pinned edges of the substrate. This can be found back in the results shown in figure 3.33. All three show a sharp up-tick at a time of roughly 170 ps or 0.8 nm in depth, which is approximately the time at which the edges start to come into contact. The results beyond that depth should then be disregarded as they do not match the intended conditions. Therefore the hardness values will instead be taken between...
Figure 3.32: 3D views of Berkovich runs 501 (1% pinned) and 502 (5% pinned). Green atoms are indenter atoms and red atoms are pinned atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

0.7 nm and 0.8 nm rather than 1.5 nm and 1.6 nm. Which gives values of $16.7 \pm 0.7$ GPa for run 501 (the result for the equivalent conical indenter simulation, 902, was $25.0 \pm 0.2$ GPa) and $28.4 \pm 0.6$ GPa for run 502 (the result for the equivalent conical indenter simulation, 905, was $34.6 \pm 0.1$ GPa).
3.13 Reproducibility

To test how reproducible these simulations are one configuration (0% run 901) was repeated five times with only the starting velocities of the atoms changed. All the runs used the same indentation velocity, which at 2 m/s was slower than the other sets (5xx, 8xx and 9xx all used 5 m/s).

Figure 3.34 shows 3D views at maximum indentation depth of all six 0% runs (901 and 701-705). All are comparable with large dislocation loops extending across most of the substrate. Runs 701-704 all have one loop that has reached the surface and run along it until blocked by an edge or corner. The deepest point for all but run 705 is only slightly above the pinned base-layer.

Each of the plots shown in figure 3.35 has the results for runs 701-705, however, only the last two have the results from run 901 for comparison as the differing velocities means the time-force plots do not line up. The results are very similar, staying within a relatively narrow band. The greatest difference is during the middle stages of withdrawal, before the indenter starts to lose most of its contact area with the substrate. The most visible change during that time is the movement of the dislocations. This makes the exact configuration of the dislocation loops prior to withdrawal a possible explanation for those differences.

Table 3.1 has the final results for all six runs. The values as calculated are in reasonable agreement with each other, however they do fall outside the error range of any individual run. This is expected as that error only indicates the accuracy of that hardness value for that particular simulation. With each simulation being different some difference in the final values is to be expected. The final value for the full set (7xx only, 901 excluded for having a different indentation speed) is 18.7 ± 1.3 GPa. This
Figure 3.34: 3D views at maximum depth of indentation. Only atoms not in a BCC-configuration are shown. Green atoms are indenter atoms. The unpinned atoms are colour-coded by height ranging from dark blue to cyan.

Figure 3.35: Time-force (top), depth-force (middle) and depth-hardness (bottom) plots for runs 701-705 with 0% pinning of the bulk. 0% run 901 is added for comparison to the last two.
<table>
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<th>Hardness (GPa)</th>
<th>Error</th>
</tr>
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<td>0.2</td>
</tr>
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<td>701</td>
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</tr>
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<tr>
<td>705</td>
<td>20.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 3.1: Table of measured hardnesses.

shows that the error for each pinning percentage is approximately an order of magnitude larger than that for a single run.

### 3.14 Aggregated results

This section will have the aggregated results for all simulations. First there is a combined time-force plot for the full set of conical indentations, excluding the 7xx repeated set. This is shown in figure 3.36. 0% is as measured, but for each higher pinning percentage the force values have been increased by +50 nN to keep them from overlapping. The maximum is at the same point for each run, at a time corresponding to the maximum indentation depth, as is to be expected. Aside from that point the plots do not show any identical features. The small dips in force during indentation occur at different times, which indicates they are likely random and due to movement of individual (groups of) atoms and are not caused by the shape or structure of the simulation. The minimum is not at the same point for each run, it occurs earlier as the pinning percentage increases and, as mentioned in the relevant run summaries, almost disappears for high pinning percentages. The plateaus are seen in only some runs but are at a time where the pile-up takes place, indicating a possible connection.

Figure 3.37 shows the hardness-depth plots for the same set of runs as the force-time plots of figure 3.36. The offset is +25 GPa, which is not enough to prevent overlap at low depth. This is intentional, both because the offset would have to be impractically large to avoid overlap and to show that the initial sharp spike is always at exactly the same depth. That spike is due to the surface layer. After the subsequent dip there follows a generally lower double spike due to the next layer. After that it tends to level out, except for the high pinning percentage runs (most clearly visible for the 100% run) where there is a steady increase. This increase may be due to the unpinned top layer which forms a decreasing proportion of the extra atoms the indenter affects as the indentation depth increases.

Finally table 3.2 lists the measured hardness for each simulation and figure 3.38 has the hardness set out against the percentage of atoms pinned. The values show a steady, but apparently non-linear, increase in hardness for each increase in pinning percentage. A line has been fit through the main set of conical indenter points (runs 803 and 9xx) for guidance. The equation describing the fit is \[-57 \cdot \exp(-0.056 \cdot x) + 78\] which has a RMS (root-mean-square) error of 1.3. The two points for the Berkovich indenter type are also shown in figure 3.38. As can be seen, they are both somewhat lower than the equivalent conical indenter points but they appear to follow the same trend.
Figure 3.36: Aggregated force-time plot. They are in order of increasing pinning percentage starting with 0%. Each new plot is offset by +50 nN.

Figure 3.37: Aggregated hardness-depth plot. They are in order of increasing pinning percentage starting with 0%. Each new plot is offset by +25 GPa.
<table>
<thead>
<tr>
<th>Run Nr.</th>
<th>Indenter type</th>
<th>% pinning</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>701</td>
<td>Cone</td>
<td>0%</td>
<td>18.8 ± 0.2</td>
</tr>
<tr>
<td>702</td>
<td>Cone</td>
<td>0%</td>
<td>16.8 ± 0.2</td>
</tr>
<tr>
<td>703</td>
<td>Cone</td>
<td>0%</td>
<td>18.0 ± 0.1</td>
</tr>
<tr>
<td>704</td>
<td>Cone</td>
<td>0%</td>
<td>19.5 ± 0.2</td>
</tr>
<tr>
<td>705</td>
<td>Cone</td>
<td>0%</td>
<td>20.6 ± 0.1</td>
</tr>
<tr>
<td>901</td>
<td>Cone</td>
<td>0%</td>
<td>21.6 ± 0.2</td>
</tr>
<tr>
<td>902</td>
<td>Cone</td>
<td>1%</td>
<td>25.0 ± 0.2</td>
</tr>
<tr>
<td>904</td>
<td>Cone</td>
<td>2%</td>
<td>28.2 ± 0.2</td>
</tr>
<tr>
<td>905</td>
<td>Cone</td>
<td>5%</td>
<td>34.6 ± 0.1</td>
</tr>
<tr>
<td>906</td>
<td>Cone</td>
<td>7%</td>
<td>37.7 ± 0.2</td>
</tr>
<tr>
<td>803</td>
<td>Cone</td>
<td>10%</td>
<td>46.2 ± 0.2</td>
</tr>
<tr>
<td>907</td>
<td>Cone</td>
<td>15%</td>
<td>52.3 ± 0.2</td>
</tr>
<tr>
<td>908</td>
<td>Cone</td>
<td>20%</td>
<td>59.8 ± 0.2</td>
</tr>
<tr>
<td>909</td>
<td>Cone</td>
<td>25%</td>
<td>63.5 ± 0.1</td>
</tr>
<tr>
<td>911</td>
<td>Cone</td>
<td>100%</td>
<td>200.2 ± 0.2</td>
</tr>
<tr>
<td>501</td>
<td>Berkovich</td>
<td>1%</td>
<td>16.7 ± 0.7</td>
</tr>
<tr>
<td>502</td>
<td>Berkovich</td>
<td>5%</td>
<td>28.4 ± 0.6</td>
</tr>
</tbody>
</table>

Table 3.2: Table listing the measured hardness for all runs.

Figure 3.38: Aggregated results for all simulations with the percentage of points pinned set out against the hardness measured.
Chapter 4

Discussion

The discussion of the results will begin with a short overview of the study. This is followed by a discussion of some of the findings described in chapter 3, grouped by simulation set. The last section discusses comparisons between these simulations and simulations and experiments done by others.

4.1 Overview

This study consisted of seventeen separate simulations, divided over three sets: set 7xx, consisting of five identical simulations to test how reproducible the results of a simulation are; set 9xx, which is the main body of work, has ten simulations ranging from zero to all substrate atoms pinned and, like the 7xx series, uses a conical indenter. The last set, 5xx, has only two simulations and uses a different indenter shape.

The overall conclusion is that the addition of pinned atoms resulted in an increase in measured hardness. That increase is correlated with the percentage of points pinned but the relationship is not linear (see figure 3.38). The increase in hardness is also significantly larger than the difference between different simulations using the same conditions.

Figures 2.1 and (a subset of) 3.38 are reproduced next to each other in figure 4.1 for comparison. The hardness scales differ as figure 4.1a uses the Vickers scale. Figure 4.1a is also based on macroscopic indentations instead of the nano-indentations used in 4.1b. Due to these different scales no direct comparisons are possible, however relative changes may still be compared (the range of the y-axis in figure 4.1b is as close as possible to 1/3 that of figure 4.1a). The figures show that the changes in hardness due to pinning in the simulations are somewhat similar to that of Ni in Ferrite, though with an approximately 75% increase versus the approximately 100% increase for Ni, the change is not quite as large.
4.2 Runs without pinned atoms

The first discussion points come from the runs without any pinned atoms in the substrate, these are runs 901 and 701-705.

Firstly, the forces acting on the pinning point anchors due to the random movement of the atoms at room temperature are orders of magnitude smaller than the forces due to indentation, even before any pinning points are introduced in the bulk of the substrate. This is as expected since for a crystal in a stable configuration those forces average to zero, with only very small oscillations.

Secondly, the spring-constant was high enough to both keep the substrate in place and keep the indenter intact and undistorted during indentation. If the force is too weak no indentation would take place as the indenter would simply spread out over the surface. Too strong a force would have no effect on the 0% runs discussed here but would show as a dramatic increase in hardness for even a single pinning point in the indented area. That is also why the standard method of fixing pinned atoms to their anchor-points without the use of springs would be unsuitable for this study. If neither the indenter atoms nor the substrate atoms can move outside their assigned path, the force needed for the indentation increases immensely if even a single pinned substrate atom is in the path of the indenter.

Thirdly, this set of runs demonstrates some of the side effects of only being able to use one type of atom, in this case Fe. Besides the impurities that turn iron into steel which this study is attempting to substitute by pinning atoms, any iron based substance will form an oxide layer if exposed to air. As there is no oxide layer in the simulations the atoms are very 'sticky'. This is clearly visible in both the coverage of the indenter and the tendrils that form between the indenter and the substrate. Aside
from the difference in hardness of the oxide and the transition layer compared to that of pure Fe, there
should be no effect on this particular simulation, as the question is about the change due to pinning.
The ‘stickiness’ only plays a measurable role during the removal of the indenter since the initial contact
is only a single atom.

The repeated set (701-705, also 0% pinned) also shows that the simulation is broadly speaking repro-
ducible but only up to a point as the final hardness values vary by a few GPa. This is far greater than
the uncertainty for a single run but, as becomes clear for the runs with greater than 0% pinning, it is
less than the difference between runs due to pinning.

4.3 Runs with pinned atoms

For the full set of conical indenter runs (701-705, 901-911) there are some additional points worth
noting. To start with there are the two known issues with the test setup.

Firstly, the random pinning points do not occur in the top two atomic layers, nor in a partial layer just
above the base pinning layer. This is only obvious in the high pinning percentage runs, in particular
in the final 100% run (see figure 3.30). The partial layer near the bottom is inconsequential, but the
top layer means that the hardness is different for the first few atomic layers than it is for the bulk.
While those values are discarded anyway because of the difficulty in determining the indenter area,
this error may also be responsible for a feature seen only in the higher pinning percentages. For the
higher pinning percentages the hardness tends to show an increase as the depth increases. As the
depth increases the proportion of the indenter interacting with the unpinned surface layer compared to
the (partially) pinned lower layers decreases. It is quite likely that the increase in hardness is caused
by this shifting ratio. The top layer having a different hardness was unintended but it does model a
top layer that is sometimes present in physical experiments, though oxide layers normally have higher
hardness not lower.

Secondly, there can be pinned atoms inside the indented area. As seen in many of the runs, any pinned
atoms inside the area that the indenter moves through do not move significantly from their original
position, even when the indenter occupies the same space. This is useful for the atoms in the indenter
as it allows it to maintain its shape throughout the indentation, however it is less beneficial in the case
of the substrate atoms. Any of these atoms pinned to a location where the passage of the indenter
has left a gap remain floating in vacuum. Aside from the visual aspect of there being floating atoms
where there should be none, there are other potential problems. During both the indentation and the
withdrawal those atoms are exerting force on the indenter in a way that cannot be isolated from the
total measurement, thus resulting in higher measured hardness than otherwise. Less of an issue, but
still of interest, are the possible changes in structure after withdrawal due to the crystal regrowing
towards the pinned atoms. This second point is most visible in figure 3.17, which is of run 803 with
10% pinned, where there are two small spikes where the crystal has regrown to include what would
otherwise be floating atoms.

The results confirm the original hypothesis by showing clearly that the measured hardness is affected
by the percentage of atoms pinned and clarifies some mechanisms that are contributing to this effect.

In most of the runs that are part of this set of simulations there is a contribution from pinned atoms
inside the indented area. As pointed out in the last paragraph, these atoms do not behave in a realistic
way. Fortunately, this is not the only thing that causes the increase in hardness for an increase in pinning percentage, since most of the low pinning percentage runs do not have any atoms pinned inside the indented area but do still show a pinning percentage dependent increase in hardness. In addition, the number of atoms pinned inside the indented area is not directly related to the pinning percentage, especially for the <15% runs, and so the pinning percentage-hardness curve from figure 3.38 would be expected to be considerably less smooth. That said, for the extreme case of 100% run 911 it is presumably the primary effect.

There is also clearly a decrease in both the number and the size of the dislocation loops with an increase in pinning percentage. In all the 0% runs there are multiple large, or at least large relative to the size of the simulation, dislocation loops. The very low pinning percentages, 1% run 902 and 2% run 904, still show dislocation loops but they are smaller and appear to be hemmed in by the small number of pinned atoms. This decrease in dislocation mobility is how hardness increases in real world materials and it is therefore reasonable that the same mechanism would produce an increase in hardness in these simulations[20].

All runs demonstrate plastic deformation at the indentation site, in the sense that, after the indenter is removed, there is a crater left behind in the substrate at the point of indentation. However, most runs do not show any other forms. All the dislocation loops dissolve again during withdrawal and there are no faults other than the crater. The exception is 15% run 907, where there is a small disturbed cluster of atoms in the reformed substrate. It appears that some of the atoms pushed to greater depth by the indenter have become stuck inside a clump of atoms that is surrounded by enough pinned atoms to keep the construction stable.

The range of pinning percentages measured runs from 0% to 100% but it is clear that any simulation with a large percentage of the atoms pinned will bear little relation to what happens in reality. The high percentages were included, primarily, to see what would happen and, secondarily, to see if there was an obvious turning point at which the behaviour would change to something clearly unrealistic. There was no truly obvious point, 100% run aside. However, the complete disappearance of dislocation loops could be seen as a boundary, in which case only the simulations with <10% pinned atoms, represented reasonable conditions.

4.4 Berkovich runs

Since many hardness scales rely on using a specific indenter shape and the most common one for nano-indentation is a Berkovich indenter, one was included for easier comparisons with experiments. Due to its shape it proved highly impractical for use in simulations. Those results that could be achieved were somewhat consistent with those from the conical indenter but systematically slightly lower. This is probably due to the top layer error (see page 4.3), since the exceedingly obtuse tip interacted relatively speaking more with the top layer than the conical indenter did, in addition to which these runs were measured at shallower depth, roughly half that of the conical indenter.

4.5 Comparisons

As mentioned in the introduction on page 5 Lu et. al. ran a pair of simulations of BCC iron with no pinning and using a completely fixed spherical indenter, which means that in this case there are no
springs between atoms and their anchor-points but instead atoms are simply fixed to their anchor-points [6]. The results of those two simulations, which differed only in the crystal orientation of the substrate, were compared to an experiment performed on low-carbon IF (interstitial free) iron, which is as close to the simulated pure, perfect Fe crystal as possible. The results of 17.4 GPa for the (010) direction and 22.6 GPa for the (111) direction match reasonably with the results of the 0% pinning simulations. The experimental value Lu et al. obtained was 24.2 GPa. This is roughly equivalent to 1% pinning, a not unreasonable result considering the differences between a real experiment and a simulation.
Chapter 5

Conclusion

5.1 Summary

This study consists of a total of seventeen different simulations, which can be divided into three groups. The first is a set of five that use identical settings but use a different random drawing of the starting velocities for all the atoms. The results range from 16.8 ± 0.2 GPa to 20.6 ± 0.1 GPa, which is a spread of almost 4 GPa, demonstrating that while the simulations are somewhat reproducible the values do vary by several GPa.

Next is the main set of ten simulations covering the full range of atom pinning, starting with no atoms in the substrate pinned and finishing with all of them pinned. The results show a range from 21.6 ± 0.2 GPa for no pinned atoms to 200.2 ± 0.2 GPa for all atoms pinned. The curve that best describes the results, excluding 100%, is $-57 \cdot \exp(-0.056 \cdot x) + 78$.

Finally there are two runs using the Berkovich indenter, the results of which are 16.7 ± 0.7 GPa and 28.4 ± 0.6 GPa. These are lower than those for the equivalent conical shape runs but show the same progression.

5.2 Conclusions

Pinning a proportion of atoms, by attaching them to anchor-points with springs, certainly works as a method for increasing the hardness of a 100% Fe simulation. The increase correlates with the percentage of pinned atoms and the increase is on a reasonable scale.

Pinning more than roughly 10% of substrate atoms is probably too many, as there are no longer any dislocation loops at that point. This would mean that the possible range for iron simulations is hardness values between approximately 20 GPa and 45 GPa. That said, the 5% simulation also does not show any loops while the 7% does, so it may not be an entirely accurate cutoff point. If the simulations are changed to allow for spring breaking or spring movement (see section 5.4 Suggestions) both any limiting percentage and the total possible hardness range are almost certain to change.

Most surprising is perhaps the finding that the simulations can produce as big a spread in final hardness values as they do, for simulations that are identical apart from the particular random draw in the starting velocities of atoms. Some variation is to be expected but a range of almost 4 GPa on values.
of around 20 GPa is large. However, others have also found large differences in the end result of a simulation by only varying the starting velocities. For example Zhang et al. found in a tungsten-gold (W-Au) simulation that, by only varying those velocities, an indentation simulation may or may not leave an indentation imprint in the substrate after withdrawal.[21] That particular effect was not seen here but as both the geometry and the materials are very different this is not surprising.

5.3 Limitations

Several of the more obvious limitations of the technique as applied are simply inherited from Molecular Dynamics. The most basic of these is the scale of the simulations; due to the number of calculations involved, even the largest MD simulations, that are run on supercomputers cannot at present simulate anything approaching macroscopic scales, the largest simulations currently manage around $10^{12}$ atoms[22]. However, as it is a reasonably parallel set of calculations that, using the correct techniques, scales quite acceptably (order $O(n)$) a jump to macroscopic scales in at least one dimension is not unthinkable.

Secondly, it is only a simplified approximation of reality, the potential functions used produce reasonable results but are generally limited in their accuracy for different configurations or temperature ranges and cannot normally simulate multiple elements at once. This second point is of course the reason for this particular study, but it is important to remember that pinning points on springs are adding a further layer of abstraction on top of a pre-existing layer of abstraction.

The variation in the results produced by a single set of simulation settings is another limitation. Since it occurs even without any pinning points in the substrate it appears to be an inherent issue. It needs to be kept in mind that any targeted hardness will only be approximate.

Finally, at the moment the springs can neither move nor break. This makes having pinned points inside the indented area somewhat questionable. While the effect on the measured hardness appears to be acceptable, the effect is probably greater on the measurement of the Stiffness $S$. Stiffness is in turn a measurement of the Modulus of Elasticity $E$, another material parameter it might be of interest to be able to tweak in simulations. The stiffness is calculated from the slope of the force during the first part of withdrawal[23], which is presumably relatively heavily affected by internal pinned atoms.

5.4 Suggestions

The error whereby there are no pinned points in the top layer should be fixed. This would not be difficult, it only remains as it was not discovered until after the last run. The current value (all the following is in the main runscript, see appendix A.1) has a small offset because it uses as maximum the height of the generated crystal, neglecting the fact that the whole system is moved up by one unit later. Setting the value of $rc$ to itself +1 just before $makebt$ is run or adding 1 in the awk script where the value of $rc$ is calculated should fix it. The half-layer gap at the bottom is due to an even smaller offset introduced at the base to avoid the faintest possibility of atoms getting pinned twice, if it has to be removed (by setting the $btt$ value and the $rb$ value the same) there is no reason to believe it would cause problems as it currently works correctly for the sides despite there not being a gap.
As stated in chapter 4, the indenter does not appear to distort for any pinning percentage. With some extra work it is also possible to eliminate that concern entirely and simultaneously allow for any indenter shape. Rather than calculate what the projected area should be based on the movement of the pinning points and the shape input during the making of the indenter a small script could find that projected area. This would be done by finding the atoms in a thin slice at the ‘surface’ of the substrate that are attached to the correct type of pinning point. The coordinates of those atoms then indicate the projected area. This method was not used as it proved unnecessary in this case and there are associated downsides. The method would be orders of magnitude slower since instead of a single calculation at each time-step it would need to read in the cn-file and bt-file, find the appropriate atoms and use the coordinates to calculate an area.

Probably the largest issue with this technique is that the springs cannot break, nor can the anchor-points move. There are at least three possible solutions, given here in order of increasing complexity. First the springs could ‘snap’ if a particular level of force is exceeded. This should be relatively easy to implement, but might not be the best solution as most disturbances in the lattice, such as other atom types, cannot simply vanish from one moment to the next. The second and third options are closely related variants of each other. When the force on the spring becomes too great you could move the attached anchor-point. The choice is whether it is best to simply move it to the associated atom’s current position or to move it only enough towards the atom that the force remains at the limit but does not exceed it. The first is far simpler but may lead to a strange ‘jerky’ force-depth curve as the force from the springs gets reset to zero, builds up and is reset to zero again etcetera. The last method is more complicated to implement, requiring an extra step to calculate the new position(s), but would probably lead to the best results.

Finally, some possibilities for future studies. Firstly, the larger scale simulations and scratch tests that this technique was intended for. These are in principle possible as it is, though they would need to use a different compiler to get the larger number of atoms in the simulation and would obviously take rather longer to complete, all the simulations in this study took a relatively manageable 1-2 days each.

All the runs used the same (default) spring-constant. It would be interesting to vary this and check the effects. Should there be a difference (which one would expect to see), it could be informative to have multiple spring strengths used in the same simulation to simulate different types of barriers each with a different cut-off point for spring movement or disappearance. However these last two would require a rewrite of the relevant part(s) of Camelion.

Another interesting option would be to move away from a purely random distribution of pinned atoms and see what the effect would be of using chains or clusters of pinned atoms instead. These would require some changes in the makebt script (See appendix A.2).

Since there are a few combined potentials for Fe, allowing for two different elements in the same simulation, it might be interesting to run a simulation that is identical but where one has a subset of substrate atoms pinned, the second has the same set in the second atom type.

When only the random draw of starting velocities is changed the simulations produce varying results for the same initial settings. It would be worth finding out if and to what extent this occurs for runs that do have a percentage of substrate atoms pinned. Alternatively, but somewhat time-consuming for limited return, it would be interesting to know just how few changes need to be made to produce different results; is swapping the starting velocities of two atoms enough?
A different direction to go would be to work on another material property that can probably be tweaked in this fashion. The stiffness can be measured in the simulations in almost exactly the same way as the hardness is, except that it is not based on the total force at maximum depth but on its first derivative during indenter withdrawal. This too is quite likely to change as pinning points are added, though perhaps not as dramatically. The stiffness is in turn a measure for $E$, also known as the modulus of elasticity or Young’s modulus. Like the hardness this is an important material parameter that is currently fixed at the value for pure iron (or whichever element is being simulated) but where there is potential value in adjusting the value to match alloys.
Chapter 6

Acknowledgements

I would like to finish by giving a short thanks to some of the individuals and institutions that helped me in various ways in completing this thesis.

First, TUDelft and specifically my supervisor, Prof. Thijsse, whose knowledge and helpful discussions were key to the completion of this project. Useful discussion was also forthcoming from Dr. Nicola and Dr. Zhang.

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Of course there are also family and friends. First and foremost I still need to thank MaryRose Hoare and Cees Zeelenberg, my parents, for everything over the years. However for this project in particular I’d like to thank them for their remarkable patience, support and knowledge of English grammar. And finally I would also like to thank friends from Baracuda as well as Veronica, Laura, Aurora and Myrthe for their support.
Bibliography


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Appendix A

Scripts

A.1 Main runscript

```
set run = 901          #run number
set base = 35         #sides of crystal
set il = 0            #indenter cutoff (for flat tips)
set ih = 8            #indenter height (for real height -ih)
set is = 3            #indenter shape (1=4sided pyramid, 2=berkovich, 3=cone)
set wall = 2
set indh = 1          #indenter height above substrate
set depth = 6          #indenter max depth
set stay = 1           #indenter waiting time at depth
set vel = 25           #indenter velocity
set btt = 3            #top of fixed points for base
set btib = 0           #bottom of fixed points for indenter. Set 0 for whole indenter
set ra = 0             #chance of fp in base
set rb = 3.5           #min random base
set rc = 0             #max random base. Set 0 for whole base
set rd = 0             #chance of fp in indenter
set re = 0             #min random indenter
set rf = 0             #max random indenter
set out = 3            #forcegraph, 3 is zindenter
set rep = 1

set vel = 'ls | awk -v x=$vel 'NR==1 {print (1000/(x*0.709))}'
set maxno = 45000
set pt = 10000
```
cp makeindenter_dmod_POzruns indenterrun$run

makextal -t 3 -k $base -l $base -m $ih -d 1.13 -M 1 55.847 -v 0.3 -s 1 -U 1 > cn00$run.0
./goion_Fe_pre_indent 00$run 0 $pt $pt
dogcn 00$run $pt > temp.mi
awk
-v il=$il 
-v ih=$ih 
-v is=$is 
'NR==1 {N=$10; Lx=$11; Ly=$12; Lz=$13; T=$14; id=1; firstdone=0} 
NR<=N {z=$3; y=$2; x=$1; VL=sqrt(3)*$3*sin(3.14159/180*65.3)/cos(3.14159/180*65.3) 
if(is==1 && z>il && z<ih && (((x-sqrt((Lx/2)^2))^2<((z)^2)) && (((y-sqrt((Ly/2)^2))^2<((z)^2))) 
{if (firstdone==0) 
  {print x,y,z,$4,$5,$6,$7,id,$9,N,Lx,Ly,Lz,T; firstdone=1} 
else 
  {print x,y,z,$4,$5,$6,$7,id,$9} 
  id++} 
if(is==2 && z>il && z<ih && y<(2*(x+VL-Lx/2)-L+Ly/2) && y<(2*(x-Lx/2)+3*L+Ly/2) && y>(Ly/2-L)) 
{if (firstdone==0) 
  {print x,y,z,$4,$5,$6,$7,id,$9,N,Lx,Ly,Lz,T; firstdone=1} 
else 
  {print x,y,z,$4,$5,$6,$7,id,$9} 
  id++} 
if(is==3 && z>il && z<ih && (((x-sqrt((Lx/2)^2))^2)+((y-sqrt((Ly/2)^2))^2)<((z)^2))) 
{if (firstdone==0) 
  {print x,y,z,$4,$5,$6,$7,id,$9,N,Lx,Ly,Lz,T; firstdone=1} 
else 
  {print x,y,z,$4,$5,$6,$7,id,$9} 
  id++} 
}' temp.mi > temp2.mi

set height = 'wc -l temp2.mi | awk -v base=$base -v maxno=$maxno '{print (maxno-$1)/(base*base+2)-1)''
echo no of atoms left is 'wc -l temp2.mi | awk '{print $1}''
if (1>'wc -l temp2.mi | awk '{print $1}'' exit

makextal -t 3 -k $base -l $base -m $height -d 1.13 -H 1 -K 1 -L 1 -M 1 55.847 -v 0.3 -s 0.5 -U 1 > cn0$run.0
./goion_Fe_pre_indent 0$run 0 $pt $pt
dogcn 0$run $pt > tempb.mi
set height = awk 'NR==1 {if ($13>0} print $13} else {print -1*$13}' tempb.mi

set N = 'wc -l tempb.mi | awk '{print $1}''

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```
set diff = 'awk -v il=$il -v N=$N 'NR==1 {max=0} NR<N {if ($3>max) {max=$3}} NR
==N {print max-il}' tempb.mi'

awk -v h=$diff -v hp=$indh ' {{print $1,$2,h+hp+$3,$4,$5,$6,$7,$8,$9}}' temp2.mi > temp3.mi
cat tempb.mi temp3.mi > tempc.mi
set num = ' wc -l tempc.mi | awk '{print }' 'awk \
-v num=$num \ 
-v h=$diff \ 
-v ih=$ih \ 
-v hp=$indh \ 
' {if (NR==1) {print $1,$2,$3+1,$4,$5,$6,$7,$9,NR,9,num,$11,$12,-(h+ih+hp+5),0} \ else {print $1,$2,$3+1,$4,$5,$6,$7,$9,NR,N9}}' tempc.mi > temp4.mi
set crosheight = 'awk -v N =$N 'NR==1 {max=0} NR <= N {if ( $3>max) {max=$3}} NR == N 
{print max} ' temp4.mi'

set N = 'wc -l tempc.mi | awk '{print $1}''
set maxheight = 'awk -v N =$N 'NR==1 {max=0} NR <N {if ( $3>max) {max=$3+5}} NR==N 
{print max} ' temp4.mi'

set depth = ' wc -l tempb.mi | awk -v depth=$depth -v indh=$indh '{print depth+indh}''

set ih = 'awk 'NR==1 {if ($13>0) {print $13} else {print -1*$13}}' temp4.mi'
set btib = 'awk -v h=$height -v i=$indh 'NR==1 {print h+i}' temp4.mi'
set rc = 'awk -v rc=$rc -v h=$height 'NR==1 {if (rc >=0) {print h-rc} else {print rc}}' temp4.mi'

set last = 'wc -l temp2.mi | awk -v depth=$depth -v stay=$stay -v vel=$vel '{
print int (2*depth+vel+stay+10)*10000}'

awk -v stay=$stay -v vel=$vel -v depth=$depth 'NR==1 {stop=0.5;step=0.25;stv=step+vel;st=depth/step;print 0,0,0,0
"stay,0,0,0} NR<(2*st+1) {if (NR*step <=depth)
{print NR*(stop+stv)+stay,0,0,-NR*step"nNR*(stop+stv)+stay+stop,0,0,-NR*step
if (NR*step>depth) {print
NR*(stop+stv)+stay,0,0,-(2*depth-NR*step)"nNR*(stop+stv)+stay+stop,0,0,-(2*
depth-NR*step)}}{{print
NR*(stop+stv)+stay,0,0,-(2*depth-NR*step)"nNR*(stop+stv)+stay+stop,0,0,-(2*depth-NR*step)}}' tempc.mi>pp$run

./makebt_dmod $run 0 0 $btib $crosheight $maxheight $wall $ra $rb $rc $rd $re $rf
echo 'wc -l temp2.mi | awk -v depth=$depth -v stay=$stay -v vel=$vel '{print 2*depth+vel+3+stay}''
```

./goion_Fe_indenttest.POz $run 0 $last 50000
echo Done.
A.2 Make_bt

```bash
set run = $1
set time = $2
echo Making file bt$run from cn$run.$time
set zbl = $3
set zbh = $4
echo Bottom positions between z=$zbl and z=$zbh
# default: impossible values for top atoms
set ztl = 6.0
set zth = 5.0
set rfnum = −0.1
set rmnum = −0.1
set sw=−1

set rfmin = 3
set rfmax = 2
set rmmin = 3
set rmmax = 2

set xcen = 0
set xs = 0
set ycen = 0
set ys = 0
set zcen = 0
set zs = 0

if ($#argv >= 6) then
  set ztl = $5
  set zth = $6
  echo Top positions between z=$ztl and z=$zth
endif
if ($#argv >= 7) then
  set sw = $7
  echo Sides fixed by $sw nm worth of atoms
endif
if ($#argv >= 8) then
  set rfnum = $8
  set rfmin = $9
  set rfmax = $10
  set rmnum = $11
  set rmmin = $12
  set rmmax = $13
endif
if ($#argv >= 14) then
  set xcen = $14
  set xs = $15
  set ycen = $16
  set ys = $17
  set zcen = $18
```

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set zs = $19

echo box created at $xcen, $ycen, $zcen

echo $xs, $ys, $zs

endif

echo $1, $2, $3, $4, $5, $6, $7, $8, $9, $10, $11, $12, $13, $14, $15, $16, $17, $18, $19

awk

v zbl=$zbl
v zbh=$zbh
v ztl=$ztl
v zth=$zth
v sw=$sw
v rfnum=$rfnum
v rmnum=$rmnum
v rfmin=$rfmin
v rfmax=$rfmax
v rmmin=$rmmin
v rmmax=$rmmax
v xcen=$xcen
v xs=$xs
v ycen=$ycen
v ys=$ys
v zcen=$zcen
v zs=$zs

`NR==1 {N=$6; Lx=$7; Ly=$8; Lz=$9; firstdone=0} 
NR<N {z=$3; y=$2; x=$1; } 
if (z>=zbl && z<=zbh) 
  {printf "%.10g %.10g %.10g %d 3 ", $1, $2, z, $4; 
   if (firstdone==0) 
   {printf "%.10g %.10g %.10g", Lx, Ly, Lz; firstdone=1} 
   printf "\n"; nat++} 
if (z>zh && z<ztl && (x<=sw || y<=sw || y>=(Ly-sw) || x>=(Lx-sw))) 
  {printf "%.10g %.10g %.10g %d 3 ", $1, $2, z, $4; 
   if (firstdone==0) 
   {printf "%.10g %.10g %.10g", Lx, Ly, Lz; firstdone=1} 
   printf "\n"; nat++} 
if (x>xcen-<xs && x<xcen+xs && y>ycen-ys && y<ycen+ys && z>zcen-zs && z<zcen+zs) 
  {printf "%.10g %.10g %.10g %d 3 ", $1, $2, z, $4; 
   if (firstdone==0) 
   {printf "%.10g %.10g %.10g", Lx, Ly, Lz; firstdone=1} 
   printf "\n"; nat++} 
if (z>rfmin && z<rfmax && (x>xcen-<xs && x<xcen+xs && y>ycen-ys && y<ycen+ys && z>zcen-zs && z<zcen+zs) && x>=sw && y>=sw && y>=(Ly-sw) && x>=(Lx-sw) && rand() <rfnum) 
  {printf "%.10g %.10g %.10g %d 3 ", $1, $2, z, $4; 
   if (firstdone==0) 
   {printf "%.10g %.10g %.10g", Lx, Ly, Lz; firstdone=1} 
   printf "\n"; nat++} 


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if (z>rmmin && z<rmmax \(! (x>xcen-xs && x<xcen+xs && y>ycen-ys && y<ycen+ys && z>zcen−zs && z<zcen+zs) && x>=sw && y>=sw && y<=(Ly−sw) && x<=(Lx−sw) && rand() <rmnum) \)
{printf "%.10g %.10g %.10g %d −3 ", $1,$2,z,$4; \}
if (firstdone==0) \)
{printf "%.10g %.10g %.10g", Lx, Ly, Lz; firstdone=1}\n
printf "\n"; nat++} \nif (z>(ztl+0.01) && z<=zth) \n{printf "%.10g %.10g %.10g %d −3 ", $1,$2,z,$4; \}
if (firstdone==0) \n{printf "%.10g %.10g %.10g", Lx, Ly, Lz; firstdone=1}\n
printf "\n"; nat++} \n}

set nat = 'wc −l bt$run | awk '{print $1}''

echo bt$run created with $nat anchor points.
A.3 TimeSlices

```r
file = 901
time = c(803)
di = 1
times = c("50000", "235000", "410000", "525000", "645000", "750000")
di2 = 2
di3 = 3

for (file in files) {
  for (time in times) {
    fc <- file(paste(file, "\cn", file, ".", time, sep = ""))
    mylist <- strsplit(readLines(fc), " +")
    close(fc)
    fc2 <- file(paste(file, "\bt", file, sep = ""))
    templist <- strsplit(readLines(fc2), " +")
    close(fc2)
    btdata <- lapply(templist, as.numeric)
    cndata <- lapply(mylist, as.numeric)
    extrvals <- cndata[[1]][7:11]
    totalatoms <- cndata[[1]][7]
    datatable <- matrix(0, totalatoms, 10);
    bttable <- matrix(0, totalatoms, 4);
    for (i in 1:totalatoms) {
      datatable[i, 1:5] <- cndata[i][2:6]
      datatable[i, 6:9] <- cndata[i + totalatoms][2:5]
      sl <- max(datatable[, di])/2 - 1
      fl <- max(datatable[, di])/2 + 0.2
    }
    for (i in 1:length(btdata)) {
      w <- which(datatable[, 4] == btdata[[i]][4])
      if (length(w) == 1) {
        bttable[w, 1] <- btdata[[i]][5]
      }
    }
    T1table <- c()
    T2table <- c()
    T3table <- c()
    for (i in 1:totalatoms) {
      if (datatable[i, di] > sl & datatable[i, di] < fl & bttable[i, 1] == -3) {
        T1table <- c(T1table, datatable[i, 4])
      }
      if (datatable[i, di] > sl & datatable[i, di] < fl & bttable[i, 1] == 0) {
        T2table <- c(T2table, datatable[i, 4])
      }
      if (datatable[i, di] > sl & datatable[i, di] < fl & bttable[i, 1] == 3) {
        T3table <- c(T3table, datatable[i, 4])
      }
    }
  }
}
```

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fc <- file(paste(file, "\cn", file, ".", time, sep=""))
mylist <- strsplit(readLines(fc), " +")
close(fc)
cndata <- lapply(mylist, as.numeric)
extravals <- cndata[[1]][7:11]
totalatoms <- cndata[[1]][7]
datatable<--matrix(0,totalatoms,10);
for (i in 1:totalatoms) {
datatable[i,1:5]<-cndata[[i]][2:6]
datatable[i,6:9]<-cndata[[i+totalatoms]][2:5]
}
colla=c()
collb=c()
colla=c()
collb=c()
colla=c()
collb=c()
for (i in T1table) {
w<-which(datatable[,4] == i)
colla<-c(colla, datatable[w,di2])
collb<-c(collb, datatable[w,di3])
for (i in T2table) {
w<-which(datatable[,4] == i)
colla<-c(colla, datatable[w,di2])
collb<-c(collb, datatable[w,di3])
}
for (i in T3table) {
w<-which(datatable[,4] == i)
collb<-c(collb, datatable[w,di2])
collb<-c(collb, datatable[w,di3])
write.table(data.frame(colla, collb), file=paste(file, ",", time, ",T1.dat", sep=""),
           row.names=FALSE, col.names=FALSE, sep=" ")
write.table(data.frame(col2a, col2b), file=paste(file, ",", time, ",T2.dat", sep=""),
           row.names=FALSE, col.names=FALSE, sep=" "
write.table(data.frame(col3a, col3b), file=paste(file, ",", time, ",T3.dat", sep=""),
           row.names=FALSE, col.names=FALSE, sep=" "
        )
    )
    )
}
A.4 FTFDHDplots

directoryin="C:\\Example\\Directory\\"
directoryout="C:\\Example\\Directory\\"
files=c(901,902,803,904,905,906,907,908,909,911)
ind=1

for (file in files) {

filedata <- read.table(paste(directoryin, file, "\\pf", file, "Fe-ZW-11.53-test", sep=""));
ppdata <- read.table(paste(directoryin, file, "\\pp", file, sep=""));

step=200;


time=rep(0,floor(length(filedata[,1])/step));
force=rep(0,floor(length(filedata[,1])/step));
force_err=rep(0,floor(length(filedata[,1])/step));

for (i in 1:floor(length(filedata[,1])/step)) {

time[i] <- mean(filedata[(1+(i-1)*step):(i*step),1]) * 0.709
force[i] <- -1*mean(filedata[(1+(i-1)*step):(i*step),4])
force_err[i] <- sd(filedata[(1+((i-1)*step)):((i*step),4)]) / sqrt(step)
}
tfout <- data.frame(time, force, force_err);
write.table(tfout, file=paste(directoryout, "TF_", file, "_Z.dat", sep=""), row.names=FALSE, col.names=FALSE, sep=" ")

coor=rep(0,floor(length(unique(ppdata[,1]))));
for (i in 1:floor(length(unique(ppdata[,1])))) {

coor[i] <- which(abs(ppdata[i,1]-filedata[,1])==min(abs(ppdata[i,1]-filedata[,1])), arr.ind=T)
}
coor=unique(coor);

depth=rep(0,length(coor));
d_force=rep(0,length(coor));
d_force_err=rep(0,length(coor));
depth[1] <- filedata[1,1]*0.2684*1e-9;
d_force[1] <- -1*filedata[1,4];
d_force_err[1] <- 0;

for (i in 2:length(coor)) {

depth[i] <- 0.2684*1e-9*(-1+mean(c(ppdata[i-1,4],ppdata[i,4]))) -1);
d_force[i] <- -1*mean(filedata[coor[i-1]:coor[i],4]);
d_force_err[i] <- sd(filedata[coor[i-1]:coor[i],4]) / sqrt(coor[i]-coor[i-1]);
}
dfout <- data.frame(depth, d_force, d_force_err);
write.table(dfout, file=paste(directoryout, "DF", file, "_Z.dat", sep=""), row.names =FALSE, col.names=FALSE, sep=" ")

dhout <- subset(dfout, dfout[,1]>0)[1:which(max(dfout[,1])==subset(dfout, dfout[,1]>0), arr.ind=T),]

if (ind==1) {
  for (i in 1:length(dhout$depth)) {
    dhout$d_force[i]=dhout$d_force[i]/(3.14159*(dhout$depth[i])^2);
    dhout$d_force_err[i]=dhout$d_force_err[i]/(3.14159*(dhout$depth[i])^2);
  }
  if (ind==2) {
    for (i in 1:length(dhout$depth)) {
      dhout$d_force[i]=dhout$d_force[i]/((dhout$depth[i])^2+24.67523924);
      dhout$d_force_err[i]=dhout$d_force_err[i]/((dhout$depth[i])^2+24.67523924);
    }
  }
  write.table(dhout, file=paste(directoryout, "HF", file, "_Z.dat", sep=""), row.names =FALSE, col.names=FALSE, sep=" ")
}
A.5 OVITO Import

```r
options("scipen"=100)
directoryin="C:\Example\Directory\"
directoryout="C:\Example\Directory\"
file=c(901,902,803,904,905,906,907,908,909,911)
files=c(505)
time="500000"
times=seq(50000,2000000,50000)

for (file in files) {
  for (timet in times) {
    time <- toString(timet)
    fc <- file(paste(directoryin, file,"\cn", file,"\time", sep=""))
    mylist <- strsplit(readLines(fc), "+")
    close(fc)

    fc2 <- file(paste(directoryin, file,"\bt", file, sep=""));
    templist <- strsplit(readLines(fc2), "+")
    close(fc2)

    btdata <- lapply(templist, as.numeric)
    cndata <- lapply(mylist, as.numeric)
    extravals <- cndata[[1]][7:11]
totalatoms <- cndata[[1]][7]
datatable<-matrix(0, totalatoms, 10);
btttable<-. matrix(0, totalatoms, 4);

    for (i in 1:totalatoms) {
      datatable[i,1:5]<-cndata[[i]][2:6]
      datatable[i,6:9]<-cndata[[i+totalatoms]][2:5]
    }
    for (i in 1:length(btdata)) {
      w<-which(datatable[,4] == btdata[[i]][4])
      if (length(w)==1) {
        datatable[w,5]<-btdata[[i]][5]+5
      }
    }
    ft4 <- file(paste(directoryout, file,"\time",".dat", sep=""))
    writeLines(paste(totalatoms, "testing", sep = "\n"), ft4)
    close(ft4)
    write.table(data.frame(datatable), paste(directoryout, file,"\time", ".dat", sep=" "), append=TRUE, row.names=FALSE, col.names=FALSE, sep=" ")
  }
}
```