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Molecular Dynamics
Simulations of
Nanofriction and Wear

Devianee Mulliah

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Dr Steven D. Kenny

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# Units and their Conversions

<table>
<thead>
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<th>Parameter</th>
<th>Symbol</th>
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</table>
| Energy    | eV     | electron-volts | $1 \text{ eV/Å} = 1.602 \text{ nN}$  
$= 1.602 \times 10^{-9} \text{ N}$  
$= 1.602 \times 10^{-9} \text{ J/m}$ |
| Force     | eV/Å   | electron-volts per Angstrom | $1 \text{ eV/Å} = 1.602 \text{ nN}$ |
|           | nN     | nano-Newton | $1 \text{ nN} = 10^{-9} \text{ N}$ |
| Distance  | Å      | Angstroms | $1 \text{ Å} = 10^{-10} \text{ m}$ |
|           | nm     | nanometre | $1 \text{ nm} = 10^{-9} \text{ m}$ |
| Time      | fs     | femto-second | $1 \text{ fs} = 10^{-15} \text{ s}$ |
|           | ps     | pico-second | $1 \text{ ps} = 10^{-12} \text{ s}$ |
| Hardness  | GPa    | giga-Pascal | $1 \text{ GPa} = \frac{1}{160.2} \text{ eV/Å}^3$ |
ABSTRACT

This thesis presents simulations of nanometre-scale ploughing friction and wear behaviour when a pyramidal diamond indenter is ploughed through the surface of bcc and fcc metals and semiconductors. Parallel molecular dynamics (MD) simulations of nanoindentation followed by nanoscratching using Newtonian mechanics have been employed to investigate the different friction mechanisms occurring at the atomic scale. Three models have been developed to carry out our investigations on nanofriction, namely the steady-state model, the spring model and the finite temperature model. Each model allows the study of distinctive aspects of atomic-scale friction. For instance, the steady-state model was employed to study the behaviour of the friction coefficient, contact pressure and scratch hardness of a silver surface as a function of depth. The effect of indenter orientation has also been investigated with results showing a diverse range of pile-up behaviour. The work material undergoes both elastic and plastic deformation during the scratching and we have studied these to analyse the origins of friction.

The spring model and the finite temperature model have been employed to investigate the stick-slip phenomenon at a low temperature of 0 K and at room temperature (i.e. 300 K), respectively. The dynamics of the indenter and the substrate, including the behaviour of the different forces in action and the coefficient of friction, at particular stick and slip events have been studied. The variation of the sliding speed and indentation depth and their effects on the occurrence of the stick-slip events has also been investigated.

Some qualitative comparisons have been made between the results from the simulations and experiments where possible. Due to available computer power, feasible indentation depths and scratch lengths were an order of magnitude smaller than experiment, while simulation times were several orders of magnitude shorter. The MD simulations, however, gave a good description of nanoindentation and nanoscratching and correlated well with the experiments.
Chapter 1

General Introduction

1.1 Simulation and Techniques

Simulation is a method used to study the dynamics of systems. Here, the term 'system' is used to mean a group of units which operate in some interrelated manner. The behaviour of a system as it evolves over time is studied by developing a simulation model. A simulation model may be a physical model, a mental conception, a mathematical model, a computer model, or some combination of all of these. Simulation can be used to study systems in the design stage, before such systems are built. Thus, simulation modelling can be used both as an analysis tool for predicting the effect of changes to existing systems, and as a design tool to predict the performance of new systems under varying sets of circumstances.

Since physical models are often relatively expensive to build and unwieldy to move, mathematical models are often preferred. In a mathematical model, mathematical symbols or equations are used (instead of physical objects) to represent the relationships in the system. To perform a simulation using a mathematical model, the calculations indicated by the model's equations are performed over and over to represent the passage of time (in one-second in-
tervals, for example). If these calculations have to be performed by hand, simulation can be extremely tedious and costly. In the sixteenth century, men spent years performing numerical simulations for creating navigation simulations but great importance of navigation to trade and naval power made the extensive effort worthwhile.

In the last fifty years, computer simulation has replaced simulation using hand calculations. Since the development of computers, the cost of arithmetic computations has halved approximately every two years and is likely to decline at this rate for at least another decade. This decline means that simulation, once a rare and expensive way of solving problems, is now very inexpensive [1].

One of the main reasons to explain why computer simulation is becoming important in physics is that most of our analytical tools such as differential calculus are best suited to the analysis of linear problems. For example, we have learnt to analyse the motion of a particle attached to a spring by assuming a linear restoring force and solving Newton's second law of motion. However, many natural phenomena are non-linear, and small changes in a variable can produce large rather than small changes in another variable. Since non-linear problems can be solved by analytical methods only in special cases, the computer gives us a new tool to explore non-linear phenomena [2].

One of the most widespread uses of computer simulation is in materials science [3] and there is a wide range of atomistic modelling methods available. These methods represent a compromise between analytic models and experiment. Two of the routinely utilised techniques are Monte Carlo (MC) [4] and molecular dynamics (MD) [5]-[6]. Physical material properties are also being calculated from first principles and this is all due to the rapid development of more powerful computers. Quantum mechanical methods like ab initio [7] and tight-binding [8] describe the material at the electronic level by solving
1.1 Simulation and Techniques

approximations to Schrödinger’s equation. These methods are important in
the study of materials phenomena. However, one shortcoming of these first
principles methods is the restriction on the size of the systems due to the com-
plexity of the calculations involved. Although MC and MD approaches allow
the use of larger system sizes compared to the first principles calculations, they
are not as accurate as the latter methods.

MC simulations are typically applied to problems having a probabilistic
basis. The first MC computer simulations were applied to the study of dense
liquids in 1953 by Metropolis et al. [9]. The first reported MD computer sim-
ulations were performed in 1956 by Alder and Wainwright [10] to study the
dynamics of hard spheres. Molecular dynamics computer simulation is a rather
straightforward approach, where given a set of initial conditions and a way of
describing interatomic forces, one simply integrates the classical equations of
motion. One important MD simulation was published in 1960 by Vineyard
et al. [11], where the authors performed a study of radiation damage in crys-
talline copper. In 1964 Rahman reported the initial MD simulation of a real
liquid [12]. The first MD simulations were restricted to modelling a very small
number of atoms, of the order of hundreds. However, recent developments in
modelling interatomic interactions has made it possible to study a wide range
of systems and processes using large-scale MD simulations [13]. Addition-
ally, modern parallel architectures allow the employment of systems involving
millions of atoms to be studied.

Our interest in this thesis lies in the investigation of the atomic scale
ploughing friction and wear behaviour between a diamond indenter and a
substrate, which can either be a metal or a semiconductor. Analytic models
have had a long history in the study of friction, which began with the work
of Tomlinson [14] and Frenkel and Kotorova [15], through to recent studies
by McClelland and Glosli [16], Sokoloff [17]-[20], and others [21, 22]. These
theoretical models have been able to simplify the complicated motions that create friction and catalogue them into basic components [13]. Our knowledge of friction and related phenomena at the atomic scale has rapidly advanced over the last decade with the development of new and powerful methods [13]. The surface force apparatus (SFA), for example, has provided new information related to friction and lubrication for many liquid and solid systems with unprecedented resolution [23]. Techniques, such as the friction force and atomic force microscopes (FFM and AFM) [24]-[27] and the quartz crystal microbalance (QCM) [28, 29] have provided new insights into the origin of friction. First-principles total-energy techniques have also been employed in the study of atomic-scale friction [30]. The results of these studies have revolutionised the study of friction, wear, and mechanical properties, and have changed many of our ideas about the fundamental origins of friction.
Chapter 2

Theory of Friction

2.1 Introduction

Tribology is the science and technology of interacting solid surfaces in relative motion and it is a very important field technologically [31]-[33]. Tribology deals with the transfer of forces from one surface onto another and it includes the study of lubrication, friction and wear. Despite being one of the oldest applied technologies, e.g., the use of firerods by the Neanderthals dates back to 200,000 B.C and the laws of solid friction were formalised by Amontons and Coulomb almost 300 years ago [34], tribology can still be viewed as a 'young' field considering the important progress made recently. The interest in tribology is purely practical: to move mechanical pieces past each other as easily as possible. By most recent estimates, improved attention to tribology would save the USA over $400 billion annually which is equivalent to 6% of their gross national product [32].

In this thesis, we concentrate mainly on friction and wear, particularly abrasive wear where a rough hard surface ploughs through a softer surface making a groove. Friction can be defined as the resistance to the sliding of one solid body over or along another, whereas wear is the progressive loss of
material when two surfaces undergo relative movement under load [35]. However, at the atomic scale these two distinctions become blurred. Friction on the atomic-scale can also be regarded as an atomic collision phenomenon and at this level can differ considerably from macroscopic friction because there are several factors that might affect the macroscopic friction but will not affect the atomic-scale friction and vice versa. While macroscopic friction between two solids, one sliding over another, can be readily measured, little is known about atomic mechanisms by which the frictional forces are generated. Furthermore, it appears that solid friction results from a combination of very different processes, such as the geometric locking of two surfaces, elastic and plastic deformations, wear, lubrication, adhesion, and so on [32]. All these processes occur on very different length scales: on the nanometre scale, atomic and molecular interactions take place, whereas the largest tribological length scales are related to the stick-slip motion of tectonic plates resulting in earthquakes. The difficulties encountered in tribology are not so surprising taking into account the diversity of phenomena which in principle can contribute to the process of friction. In fact, for a detailed understanding of friction the precise nature of the surfaces and their mutual interaction have to be known. The main challenge of modern tribology is to develop a fundamental understanding of solid friction, which will allow us to bridge the different length scales and properly relate the atomistic processes with the macroscopically observed phenomena.

Within the past decades, the interest in the microscopic mechanisms of tribology has been increasing and a research field called nanotribology [36] has emerged. This has been motivated by the appearance of experimental techniques such as the atomic force microscope (AFM). Krim [37] discusses progress in the study of friction's atomic level origins, with emphasis on the role of surface science.
2.2 Contact Mechanics

Progress in nanotribology is essential to all areas of friction and current technology has brought us to the point where we can begin to investigate atomic scale processes at sliding interfaces. As the dimensions of the components and loads used continue to decrease, scratching/wear and mechanical properties of solid surfaces and surface thin films at the micro- to nanoscale become very important, as these affect the tribological performance of surfaces. Micro/nanotribological studies are needed to develop a fundamental understanding of interfacial phenomena on a small scale and to study interfacial phenomena in the micro- and nanostructures used in magnetic storage systems, microelectromechanical systems and other industrial applications [13, 38]. The nanoscratching technique is used for studying the friction and wear processes of micro- and nanostructures [13], and can also provide information on the scratch hardness of small-scale materials. Scratch hardness is the oldest form of hardness measurement and was probably first developed by mineralogists [39].

2.2 Contact Mechanics

When two solid surfaces are loaded together there will always be some elastic or plastic deformation of each of them. Such distortions in the surface profile of the components can be viewed at two different scales, i.e. macroscale and microscale. At a relatively macroscopic scale, the degree of flattening of the two curved surfaces in contact can be expressed as a proportion of their radii. However, on the microscopic scale a real surface is not truly smooth. It therefore follows that when two solid bodies are pushed into contact at the microscopic scale they will initially touch at a discrete number of points or asperities (see Section 2.4).

To develop relationships between indentation measurements and mechani-
Theory of Friction

cal properties of the tip and the substrate samples, several models have been used which describe the contact between two elastic materials. These models include the Hertzian, Derjaguin-Muller-Toporov (DMT), Burnham-Colton-Pollock (BCP), Johnson-Kendall-Roberts-Sperling (JKRS) and the Maugis models. We shall briefly outline three of these models, namely, the Hertzian, DMT and JKRS models in the following sections. The reader is referred to Ref. [13] for an explanation of the other two above-mentioned models.

2.2.1 Hertzian Contacts

When any two curved bodies of different radii of curvature are brought into contact they will initially touch at either a point or along a line. With the application of the smallest load, elastic deformation enlarges these into contact areas across which the loads are distributed as pressures. The first analysis of this situation was presented by Heinrich Hertz in 1881 [36]. Neither surface forces nor adhesion hysteresis are assumed in the Hertzian theory.

Let two solids of radius $R_1$ and $R_2$ be in a point contact, as shown in Fig. 2.1(a). We assume that the two bodies are filled with uniform isotropic linearly elastic media characterised by Young's moduli $E_1$, $E_2$ and Poisson ratios $\mu_1$, $\mu_2$. If the bodies are compressed by some force $F_y$, then according to Hertz's classical equations [40] they will at first deform elastically. Thus, as a result of the compression they become deformed and approach each other within a small distance $h$ (Fig. 2.1(b)). Then the contact area will not be a point but a surface portion. According to Hertzian contact mechanics, the contact area is a circle of radius $a$, which is given by

$$a = F_y^\frac{1}{3} \left[ \frac{1}{K} \frac{R_1 R_2}{R_1 + R_2} \right]^\frac{1}{3},$$

(2.1)
where $K$ is the effective Young's modulus and is given by

$$\frac{1}{K} = \frac{3}{4} \left[ \frac{1 - \mu_1^2}{E_1} + \frac{1 - \mu_2^2}{E_2} \right]. \quad (2.2)$$

Figure 2.1: (a) The contact between two curved bodies of radius $R_1$ and $R_2$ before deformation. (b) Deformation undergone by the two bodies. The surfaces before deformation are shown by the dotted line and the squeezed surfaces are shown by the full line.

Hertz, therefore, found a relation between the deformation of the surface and the applied load $F_y$, which can be written as

$$F_y = \frac{K a^3}{R}, \quad (2.3)$$

where

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \quad \text{and} \quad R = \frac{R_1 R_2}{R_1 + R_2}. \quad (2.4)$$

Moreover, Hertz found that the relationship between the contact radius $a$ and
the penetration depth, \( h \), is given by

\[
h = \frac{a^2}{R}.
\]  

(2.5)

Hence, the penetration \( h \) can be written as the following expression:

\[
h = F_y \left[ \frac{1}{K^2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \right]^{\frac{1}{3}}.
\]  

(2.6)

So \( h \propto F_y^{\frac{2}{3}} \) and correspondingly \( F_y \propto h^{\frac{3}{2}} \). This dependence of \( F_y \) on \( h \) is valid for all bodies of finite dimensions.

2.2.2 The DMT Mechanics

The DMT equations were formulated by Derjaguin, Muller and Toporov in 1975 [41, 42] and they take the following form

\[
F_y = \frac{K a^3}{R} - 2\pi R \varpi,
\]  

(2.7)

and

\[
h = \frac{a^2}{R},
\]  

(2.8)

where \( \varpi \) is the work of adhesion evaluated at contact. DMT mechanics is most appropriate for rigid systems, where adhesion between the system is low and their radii of curvature are small. This model accounts for long-ranged attraction around the boundary of the contact area, but constrains the tip-sample geometry to remain Hertzian. In other words, DMT is Hertz with an offset due to surface forces and so the DMT model reduces to the Hertz model if \( \varpi = 0 \).
2.3 History of Friction

2.2.3 The JKRS Mechanics

This model was developed by Johnson, Kendall, Roberts and Sperling [43, 44]. Here, there are no forces between the surfaces when they are not in contact but upon contact short-ranged attractive forces suddenly operate within the contact area. Also, the tip-sample geometry is not constrained to remain Hertzian. The contact geometry is allowed to be severely deformed. The equations for the JKRS analysis are

\[ F_y = \frac{K a^3}{R} - \sqrt{6\pi\omega K a^3}, \quad (2.9) \]

and

\[ h = \frac{a^2}{R} - \frac{2}{3} \sqrt{\frac{6\pi\omega a}{K}}. \quad (2.10) \]

The JKRS model works well for systems where the adhesion is large and that have large radii of curvature and low stiffness. If we set \( \omega = 0 \) in Eqs. 2.9 and 2.10, the JKRS model reduces to the Hertz model.

2.3 History of Friction

Primitive man was conscious of the role of friction since he was aware of the fact that a spherical object will move more readily than a flat one. But one does not know if the act of rubbing pieces of wood together to produce fire was discovered by accident or from some vague notion that rubbing generates heat since in cold climates, human beings generally rub their hands to produce warmth.

The first recorded systematic study in the field of tribology is due to Leonardo da Vinci (1452-1519) at the beginning of the 15th century as one of the first scholars to study friction. He not only performed experimental studies of friction, but also developed bearing materials, studied wear and presented
ingenious schemes for rolling-element bearings. He measured the force of friction between objects on both horizontal and inclined surfaces. He stated the two basic laws of friction 200 years before Newton even defined what force is and these laws can be summarised as: (1) friction is independent of the contact area, and (2) if the load of an object is doubled, its friction will also be doubled. He observed that different materials move with different ease and he therefore concluded that this was a result of the roughness of the material in question, i.e. smoother materials will have smaller friction. Leonardo Da Vinci did not publish his theories, so he never got credit for his ideas. The only evidence of their existence is in his vast collection of journals.

The two basic laws of friction that had been discovered by Leonardo Da Vinci, were later re-discovered by Amontons (1663-1705). The latter also came up with an original set of theories: friction was predominately a result of the work done to lift one surface over the roughness of the other, or from the deforming or the wearing of the other surface. For several centuries after Amontons' work, scientists believed that friction was due to the roughness on the surfaces. In the 18th century, Coulomb (1736-1806) added the following to the second law of friction: “strength due to friction is proportional to compressive force” and “although for large bodies friction does not exactly follow this law”. Coulomb published the work referring to Amontons. The second law of friction is known as the Amontons-Coulomb Law, referring to the work done by the two scientists in 1699 and 1781, respectively. The Amontons-Coulomb law of friction holds for many different material combinations and geometries but unlike Newton's first law, nothing fundamental can be derived from it.

In 1950, Bowden and Tabor gave a physical explanation for the laws of friction. They determined that the true area of contact is a very small percentage of the apparent contact area. The true contact area is formed by the
asperities. As the normal force increases, more asperities come into contact and the average area of each asperity contact grows. The frictional force was shown to be dependent on the true contact area, which is a much more satisfying argument than that stipulated by the Amontons-Coulomb law. Bowden and Tabor argued that all the dynamics of friction take place within these asperities. The friction hypothesis from dragging one surface up the roughness of the other surface was dismissed.

Further study on friction is now concentrated on microscale contacts formed between single and multiple asperities, where deformation and adhesion are considered. The invention of the atomic force microscope (AFM) by Binnig, Quate and Gerber in 1986 [24] enabled scientists to study friction at the atomic scale.

2.4 Nanofriction - Friction on the nanoscale

The three basic laws of friction can be summarised as follows:

(I) Friction is proportional to the load (i.e., to the applied normal force),
(II) Friction is independent of the apparent area of contact,
(III) Sliding friction is independent of the sliding velocity.

Laws I and II were found by Amontons in 1699, whereas law III was found by Coulomb in 1781. These three laws are obeyed extremely well on the macroscopic scale for dry friction (i.e. in the case of friction without lubrication, which is also called Coulomb friction). Nevertheless, they could not be derived from microscopic principles up to now. The surfaces of materials that we generally consider to be very smooth are revealed as having rough uneven surfaces when viewed through a microscope. These surface irregularities are commonly called asperities. All surfaces possess hills and valleys so that a load at the interface is only supported at suitably oriented high spots, resulting in
micro-areas, which when added together form the true area of contact. Thus, when two solid surfaces are placed in contact, the actual contact takes place at the tips of the asperities or surface irregularities and this is illustrated in Fig. 2.2. These asperity regions initially deform elastically, and, if the load is sufficiently high, they deform plastically until the load can be supported; that is, the real contact area continues to increase with deformation until the contact area is sufficient to support the load applied to the two surfaces in solid-state contact.

![Figure 2.2: Two solid surfaces making contact at the tips of four asperities or surface irregularities. $F_x$ is the load applied tangentially and $F_y$ is the normal load.](image)

Today the tolerances of many components, such as optical devices, computer chips, and ultra-smooth surfaces, are approaching the atomic length scale. To fabricate such precise components, we require an atomic-scale understanding of the fundamental processes of surfaces in relative motion. With the advent of the newly developed scanning probe microscopes (SPMs), particularly the atomic force microscope (AFM), it is possible to study the interfacial phenomena at a small scale and light load. The AFM tip simulates a sharp single asperity travelling over a surface. Scratching and wear processes at different normal loads are studied in AFMs by using a sharp diamond tip.
Furthermore, the achievement of higher recording densities requires smoother surfaces. The ultimate objective is to use two smooth surfaces in contact for recording provided the tribological issues can be resolved. Smooth surfaces lead to an increase in adhesion, friction, and interface temperatures. Friction and wear issues are resolved by appropriate selection of interface materials and lubricants, by controlling the dynamics of the head and medium, and the environment. Hence, a fundamental understanding of the tribology of the magnetic head-medium interface becomes crucial for the continuous growth of the magnetic storage industry.

2.5 Atomic-scale studies of friction

Friction is not a very simple and well understood subject, and thus a lot of research has been done and is still going on, especially on the atomic-scale friction. As a result, some theories such as the surface roughness theory, the adhesion theory [45] and friction due to molecular interactions have been put forward to shed light on the origin of friction [46].

2.5.1 Experimental Review

Understanding material properties at the nanoscale is crucial to developing the fundamental ideas needed to design new coatings with tailor-made friction and wear properties. One of the ways in which these properties is being characterised is through the use of the AFM [13]. The AFM has enabled much research to be carried out on atomic scale friction [25, 47] and techniques using a quartz-crystal microbalance have been utilised to probe sliding friction effects [28]. Mate et al. [25] have performed experiments using the AFM which has led to the observation of a frictional force resolved on the atomic scale. Furthermore, Carpick and Salmeron [27] have observed the stick-slip
phenomenon in the motion of the AFM tips.

2.5.2 Theoretical Review

The interactions that occur at a tip-surface sliding interface (analogous to an AFM experiment) have also been investigated using MD. This has been rendered possible through the rapid development in computer technology, which has provided the means for doing large-scale simulations. Computer simulation has proven to be a valuable tool for interpreting experimental results and for suggesting new experiments and MD simulation is a very useful tool in studying indentation, adhesion, friction, fracture, surface defects and cutting on the atomic scale [48]-[55]. Furthermore, simulations provide a testing ground for simpler approximate theories. In this way, simulations can help establish the connection between experimentation and simpler models.

One advantage of simulations is that the shape of the force curve as a function of distance, along with its fine structure, can be related to specific atomic-scale events. For instance, Landman et al. [48] reported the observation of a jump to contact (JC) that corresponded to the region of the force curve where there was a rapid drop in the force just prior to tip-substrate contact. The JC phenomenon was previously observed by Pethica and Sutton [56] and by Smith et al. [57]. In that region of the force curve, the atoms of the substrate 'bulged up' to meet the tip.

Friction that arises from the contact between two solid interfaces has been investigated using both classical molecular dynamics simulations [58] and first-principles calculations [30]. Some work [46, 59, 60, 61] has been carried out to investigate different aspects of friction and numerous studies [62] have shown that friction can depend dramatically on the chemical and atomic nature of surfaces. In addition, large scale two-dimensional and three-dimensional MD simulations of the indentation and scraping of metal surfaces were carried
2.6 Layout of Thesis

out by Belak and Stowers [63]. Their simulations showed that tribological properties are strongly affected by wear or the generation of debris.

Harrison and Brenner [64] brought two (111) hydrogen-terminated diamond surfaces into contact and they used reactive potentials that allow breaking and formation of chemical bonds. Through this they were the first to observe tribochemical reactions involving strong covalent bonds in MD simulations. This showed the extreme thermomechanical conditions in sliding contacts that can induce chemical reactions. This interaction of chemistry and friction is known as tribochemistry [33]. Tribochemistry plays important roles in many processes, the best known example being the generation of fire through sliding friction.

2.6 Layout of Thesis

This thesis presents an atomic scale study of nanoindentation and nanoscratching, employing bcc and fcc metals and semiconductors as work materials. Classical MD simulations using Newtonian mechanics and many-body potentials are implemented to simulate the indentation and scratching techniques. The main objective of this work is to gain considerable insight into the different friction mechanisms and other microscopic events occurring at the atomic-scale. Qualitative comparisons between the results from experimental investigations and the simulations are made where possible. However, available computer power constrains the simulation investigations to systems that are comparatively smaller than those employed in experimental studies. Subsequently, feasible simulations performed in this work comprise of indentation depths and scratching lengths that are an order of magnitude smaller than those in experiments, while simulation times are several orders of magnitude smaller.

The pertinent details of the molecular dynamics approach and its applica-
tion to simulate the nanoindentation and nanoscratching techniques are discussed in Chapter 3. Methods that are commonly used to improve the computational efficiency, such as bookkeeping techniques, are also discussed. Moreover, an introduction is given to three parallel algorithms, namely the atom-decomposition, force-decomposition and spatial-decomposition algorithms, for classical MD in order to give the reader an insight into parallel MD simulations employed for the nanofriction investigations in this thesis. In Chapter 4, a brief introduction is given to the crystal structure of the materials considered in our work, together with a discussion on the different types of imperfections or defects in the ideal arrangement of atoms in a crystal. Three different models are employed in this thesis, namely the steady-state model, the spring model and the finite temperature model in our study of atomic-scale friction. Each model is implemented with the intent of studying particular aspects of atomic scale friction and have increasing sophistication. These three simulation models are presented in Chapter 5 where their distinct features are emphasised and discussed in a detailed manner. The results from the steady-state model are presented in Chapter 6, where the behaviour of the friction coefficient, nanohardness and scratch hardness values of fcc Ag are studied as a function of indentation depth. The effect of indenter orientation is also investigated. The spring model is employed to investigate the atomic-scale stick-slip phenomenon of a diamond tip inserted into a Ag(100) surface and the results are presented in Chapter 7. The finite temperature model is used to study the stick-slip phenomenon at a temperature of 300 K on materials with different crystal structures. The results from the simulation using the finite temperature model are analysed and discussed in Chapter 8. Finally, general conclusions are drawn in Chapter 9 and suggestions are also given for possible future work in the field.
Chapter 3

Simulation Methodology

3.1 Introduction

This chapter discusses the relevant details of molecular dynamics (MD) and its application to simulating the nanoindentation and nanoscratching (or nanofriction) processes. The discussion does not include an in-depth discussion covering the vast subject of MD, but is only a review of the most fundamental principles. For a more detailed discussion on MD, the reader is referred to Smith [5], Allen and Tildesley [6], or Haile [65]. Methods that are commonly used to improve the computational efficiency, such as bookkeeping techniques, are also discussed. In addition, an introduction is given to three parallel algorithms, namely the atom-decomposition, force-decomposition and spatial-decomposition algorithms, for classical molecular dynamics. This is to give the reader an insight into parallel MD simulations, employed for the nanofriction investigations in this thesis.
3.2 Molecular Dynamics

The two-body motion problem of the interaction of particles in a gravitational field was solved by Newton in the seventeenth century and in 1912 the Finnish mathematician, Sundman, developed a convergent infinite series that provides a solution to the three-body problem. But getting the series to converge to any useful precision requires a lot of terms and hence making the solution impractical to implement. The $N$-body problem when $N > 3$, which is the problem of finding the subsequent motions of particles as determined by classical or Newtonian mechanics, given their initial positions, masses and velocities, cannot be solved analytically. Molecular dynamics [5, 6, 65] can be described as a numerical way of solving the $N$-body problem. The solution is never exact, but if done properly it can be made arbitrarily accurate.

Molecular dynamics is a computational tool commonly used for simulating properties of solids, liquids and gases. It can be described as a computationally intensive method of studying the time-evolution of a system of $N$ discrete particles using Newton's classical equations of motion (a set of coupled ordinary differential equations). Using the MD method, the dynamic and thermodynamic behaviour of atomic assemblies may be studied, leading toward an understanding of their function and properties at the atomic level.

The wide range of characteristic times for processes that occur in the simulated systems dictates the length of time that MD simulations must be run to realistically model events of interest in these systems. Often many such simulations are necessary whenever sufficient statistics must be generated to associate microscopic characteristics with time-dependent macroscopic traits of a system.

Now, let us assume that we want to model a system of $N$ discrete particles, then in MD simulations, each of the $N$ atoms in the simulated system is treated as a point mass. The motion of the system of $N$ atoms is computed
by integrating Newton's equations and is governed by interatomic forces that depend on the location of every atom in the system. In other words, the dynamics of the system of atoms are described by assuming multiple interactions, where the forces the atoms exert on each other govern the rate and direction of motion. Atomic positions and velocities are repeatedly updated subject to this field of interatomic forces, leading to the time evolution of the (step-wise) particle trajectories. The basic feature of MD simulations is the calculation of the force on each atom and therefore the position of each atom throughout a specified period of time. The MD simulation method is deterministic, i.e., once the positions and velocities of each atom are known, the state of the system of atoms can be predicted at any time in the future or the past. This thesis is concerned with the simulation of the nanoindentation and nanoscratching processes at the atomic scale using MD simulations and it is important to point out that we use classical MD, where it is assumed that the motion of atoms in the simulated system can be modelled using Newtonian mechanics. Thus, the equation of motion for the ith atom in a system of N particles can be written as

$$F_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2}, \quad i = 1, \ldots, N$$  \hspace{1cm} (3.1)$$

where $F_i$ denotes the force acting on atom $i$, with mass $m_i$, acceleration $a_i$ and position vector $r_i$. MD computer simulations solve Newton's equations of motion for a system of $N$ discrete particles and integration of the equations of motion then yields a trajectory that describes the positions, velocities and accelerations of the particles as they vary with time.

Classical MD makes use of the Born-Oppenheimer approximation [66], which states that at every simulation step the nuclei move assuming an average distribution of electron density since electrons are much faster than nuclei. Nuclei are heavy enough to be considered as classical particles. It all allows us
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to treat nuclei as point classical particles interacting with each other by means of semi-empirical potentials, which also contain the nuclei-electron interaction on average. Thus the degrees of freedom of the electrons are not considered in a classical MD simulation. This considerable reduction in the degrees of freedom allows us to simulate systems with millions of atoms by a MD code for timescales of up to nanoseconds.

3.3 Integration Algorithms

The potential energy is a function of the atomic positions of all the atoms in the system. Due to the complicated nature of this function, there is no analytical solution to the equations of motion. Thus, the equations of motion for the system of \( N \) particles are integrated numerically by means of a suitable integration algorithm. A numerical algorithm that is symplectic is one where the error in the total energy is bounded. Such algorithms have better energy conservation properties after integrating for a large number of timesteps. A MD program requires a good algorithm to integrate Newton's equations of motion but the choice of an integration algorithm can be quite difficult. There are two main requirements that are of any real concern in a simulation code, namely, speed and accuracy. A range of algorithms have been suggested to integrate the equations of motion based on finite difference methods. The most robust low-order algorithm to have been tried and tested over many years is the Verlet algorithm [67], which is derivable from a Taylor series expansion and is symplectic. There are a variety of algorithms derived from Verlet, such as the leap-frog algorithm [68] and the velocity Verlet algorithm [69]. Another widely used algorithm is the Beeman algorithm [70], which employs more accurate terms to describe the velocity at the expense of increased computation, but this is not symplectic and total energy drift can occur.
3.3 Integration Algorithms

The time evolution of the position of atom $i$ in the Verlet algorithm is described by

$$r_i(t + \Delta t) = 2r_i(t) - r_i(t - \Delta t) + a_i(t)\Delta t^2, \quad (3.2)$$

where $a_i(t)$ is calculated by means of Eq. 3.1. Although the velocities are not necessary to find the trajectories by this algorithm, they can be useful for estimating the kinetic energy. One possible expression for the velocity, using the values of the position calculated at times $(t - \Delta t)$ and $(t + \Delta t)$, can be written as

$$v_i(t) = \frac{r_i(t + \Delta t) - r_i(t - \Delta t)}{2\Delta t}. \quad (3.3)$$

The advantage of the Verlet algorithm is that it is symplectic. One modification to the basic Verlet scheme have been proposed by Swope et al. \[71\] where the time evolution of the position and velocity of atom $i$ are given by

$$r_i(t + \Delta t) = r_i(t) + v_i(t)\Delta t + \frac{1}{2}a_i(t)\Delta t^2, \quad (3.4)$$

and

$$v_i(t + \Delta t) = v_i(t) + \frac{1}{2}[a_i(t) + a_i(t + \Delta t)]\Delta t, \quad (3.5)$$

respectively. In Eq. 3.4, $r_i$, $v_i$ and $a_i$ are the position, velocity and acceleration vectors for atom $i$ and $\Delta t$ denotes the timestep. The latter algorithm is termed the velocity Verlet algorithm and it serves to predict the positions and velocities of $N$ interacting atoms at a later point in time $(t + \Delta t)$, given the dynamical data at time $t$. Unlike the Verlet’s original version, Swope’s scheme does not need the storage of the position at the time $(t - \Delta t)$. We have employed the velocity Verlet algorithm to integrate the equations of motion in our MD code.
3.4 Outline of Molecular Dynamics

Fig. 3.1 briefly outlines the MD simulation method. Initial input parameters such as the substrate size and the total simulation time are read in. The system is then constructed; once the initial configuration of the computational box has been defined, the boundary conditions and initial velocities must be declared for every atom in the system under consideration. A spherical neighbour list is then created for each atom and the initial energies and forces are calculated. The MD simulation then enters the main loop where the dynamics of the system are allowed to evolve by the timestep by incrementing $t$ to $t + \Delta t$. The positions of the atoms at time $t + \Delta t$ are integrated using the information on the acceleration, positions and velocities of the atoms at the previous timestep $t$. After the positions of the atoms have been integrated, a check is carried out at time $t + \Delta t$ to find out which atoms are interacting and if necessary, update the neighbour lists. The force is then evaluated at the new timestep $t + \Delta t$ and the calculation of the acceleration of the atoms is then carried out. The velocities are then integrated to the time $t + \Delta t$ using the accelerations at time $t$ and $t + \Delta t$. If the motion of the atoms is damped then both the positions and velocities are adjusted according to some energy loss model. The process is then repeated to evolve the dynamics of the system to the next period in the discretised time scale by incrementing the time, until the total simulation time has been executed.

3.5 Interatomic Potentials

Newton’s equation of motion, Eq. 3.1, yields a set of $3N$ second-order differential equations that govern the dynamics, where $N$ is the number of atoms in the system. These equations can be solved with finite timestep integration methods. Most current simulations integrate for a total time of picoseconds.
3.5 Interatomic Potentials

Reads in input parameters, e.g., substrate size, simulation time, etc.

Construct system, i.e., generate computational box and define the boundary conditions

Create a spherical neighbour list for each atom and calculate initial energies and forces

Text and graphics output

Stop if total simulation time has been reached

Increment time

Integrate positions of atoms

Find which atoms are interacting and update the neighbour lists

Calculate energy and forces

Calculate acceleration of atoms

Integrate velocities of atoms

Loop over time

Figure 3.1: Flowchart outlining the basic steps involved in the MD simulation method, using the Verlet algorithm.
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to nanoseconds. The evaluation of these equations requires a method for obtaining the force \( F_i, i = 1, \ldots, N \), between the atoms. It is assumed that the potential is conservative, which implies that the interaction forces can be obtained by taking the gradient of the interatomic potential \( V \), with respect to the atomic positions. Hence, the total potential energy, \( V \), at a point \( r \) of a system of \( N \) atoms can be written as

\[
V = V(r_1, r_2, \ldots, r_N)
\]  

(3.6)

where \( r_i \) is the position vector of the \( i \)th atom with respect to the point \( r \). The force acting on atom \( i \) is taken as the gradient of the interatomic potential \( V \) evaluated at \( r_i \) and can be written as

\[
F_i = -\nabla_{r_i} V,
\]

(3.7)

where \( F_i \) denotes the force vector for atom \( i \).

Due to constraints on computer time, it is generally required that the evaluation of the interatomic forces are not too computationally intensive. Currently, there are two approaches that are widely used. In the first approach, it is assumed that the potential energy of the atoms can be represented as a function of their relative atomic positions and the forces are then obtained by taking the gradient of the potential energy with respect to atomic positions. However, the second approach is the calculation of the interatomic forces directly from first-principles or semi-empirical calculations that explicitly include electrons.

In the first approach, the potential energy function usually contains some number of free parameters which are chosen to closely reproduce some set of physical properties of the system of interest. But there are many complexities involved in developing a useful potential energy function. For example, the
parameters entering the potential energy function are usually determined by a limited set of known system properties. A consequence of that is that other properties, including those that might be key in determining the outcome of a given simulation, are determined solely by the assumed functional form. For a metal, the properties to which a potential energy function might be fit might include the lattice constant, cohesive energy, elastic constants, and vacancy formation energy. Predicted properties might then include surface reconstructions, energetics of interstitial defects, and response to an applied load [13]. For interactions between atoms where the energy rapidly decreases with increased separation, it can be assumed to be zero after a specific distance. Hence, the computational efficiency can be increased by truncating the potential at a certain cut-off distance. However, the potential energy function and some of its derivatives must be continuous to prevent energy losses from occurring. This issue is usually overcome by introducing a ‘switching’ function so that the potential energy is smoothly cut-off to zero at a specified cut-off distance. The only constraints on the potential $V$ are that it must allow a broad range of simulations to be accurately performed and permit a physically meaningful interpretation from the results. Furthermore, the calculation of the interatomic potential must be computationally feasible. Therefore, the form of the potential is crucial for efficient evaluation of the interaction forces and for the simulation to have sound predictive power.

The second approach has become more useful with the advent of powerful computers. The advantage of this approach is that the number of unknown parameters may be kept small, and because the forces are based on quantum principles, they may have strong predictive properties. The disadvantage of this approach is that the methods involved are considerably more complicated, and require more computational effort, than those used in the classical approach. Hence, longer simulation times require that both the system size and
the timescale studied be smaller than when using more approximate methods.

All the simulations performed in this thesis employed potential energy functions derived by the classical approach and hence, we will focus more on this particular approach. The simplest approach for developing a continuous potential energy function is to assume that the binding energy $E_b$ can be written as a sum over pairs of atoms

$$E_b = \sum_i \sum_{j(i)} V_{\text{pair}}(r_{ij}),$$

(3.8)

where the indexes $i$ and $j$ are atom labels, $r_{ij}$ is the scalar distance between atoms $i$ and $j$, and $V_{\text{pair}}(r_{ij})$ is an assumed functional form for the energy. Some traditional forms for the pair term are given by

$$V_{\text{pair}}(r_{ij}) = D \cdot X(X - 1),$$

(3.9)

where the parameter $D$ determines the minimum energy for pairs of atoms. Two common forms of this expression are the Morse potential ($X = e^{-\beta r_{ij}}$) and Lennard-Jones (LJ) potential ($X = (\sigma/r_{ij})^6$), where $\beta$ and $\sigma$ are arbitrary parameters that are used to fit the potential to observed properties. The short-range exponential form for the Morse function provides a reasonable description of repulsive forces between atomic cores, while the $1/r^6$ term of the LJ potential describes the leading term in long-range dispersion forces.

For systems with significant Coulomb interactions, the approach that is usually taken is to assign each atom a fractional point charge $q_i$. These point charges then interact with a pair potential

$$V_{\text{pair}}(r_{ij}) = \frac{q_i q_j}{r_{ij}}.$$  

(3.10)

Several more complex potential energy expressions have been successfully de-
3.5 Interatomic Potentials

Developed and are widely used in MD simulations, but to keep the discussion short we will concentrate mainly on the potential functions used in the simulations in this thesis. In our nanofriction investigation we have considered four different substrates, namely, silver (face-centred cubic structure), iron (body-centred cubic structure), silicon (diamond structure), and hydrogen-terminated silicon, and the potentials to model these substrates are discussed in the following sections.

3.5.1 The Embedded Atom Method Potential

For metals, the embedded atom method (EAM) and related methods have been highly successful in reproducing an array of properties, and have opened up a range of phenomena to simulation [72]–[75]. The EAM potential [76] was developed by Daw and Baskes [77] and is based on the Hohenberg-Kohn theorem which states that "the energy contribution of an atom in an array of interacting atoms is a function of the local electron density, due to all other atoms, at the position of the atom concerned." Therefore, the EAM assumes that the density of the electron gas can be approximated by a sum of electron densities from surrounding atoms, and adds a repulsive term to account for core-core interactions. Within this set of approximations, the total binding energy is given as a sum over atomic sites

\[ E_b = \sum_i E_i, \]  

(3.11)

where each site energy is given as a pair sum plus a contribution from a functional (called an embedding function) that, in turn, depends on the sum of electron densities at that site:

\[ E_i = -f(\rho_i) + \frac{1}{2} \sum_{j \neq i} V_{ij}(r_{ij}), \]  

(3.12)
where $V_{ij}(r_{ij})$ is a central pair potential representing the core-core repulsion, $f$ is an embedding function of the electron density, $\rho_i$, of atom $i$, which is approximated by the superposition of the atomic densities

$$\rho_i = \sum_{j \neq i} \phi_{ij}. \quad (3.13)$$

The summations extend over all the atoms in the system and $V_{ij}$ and $\phi_{ij}$ are functions only of the interatomic distance $r_{ij}$ and are short ranged. For a given atomic site $i$, the function $\rho_i$, in Eq. 3.13, determines the contribution to the electron density from the neighbouring atoms $j$. For practical applications, functional forms are assumed for the core-core repulsion, the embedding function, and the contribution of the electron densities from surrounding atoms. Different mathematical expressions have been proposed for the terms in Eqs. 3.12 and 3.13. The selected expression for this thesis has a Finnis-Sinclair [72] tight-binding form for the electron density, i.e.,

$$f(\rho_i) = -A \rho_i^{\frac{1}{2}}. \quad (3.14)$$

The Ag-Ag Interaction

The Ag-Ag interactions are described by Ackland’s EAM potential for silver [78], which is smoothly cut-off at 5.044 Å. According to the parameterisation of $V_{ij}$ and $\phi_{ij}$ proposed by Ackland et al., the pairwise term is given by

$$V_{ij}(r_{ij}) = \sum_{k=1}^{6} a_k (r_k - r_{ij})^3 \Theta (r_k - r_{ij}), \quad r_1 > r_2 > \ldots > r_6, \quad (3.15)$$

and the atomic density is written as

$$\phi_{ij}(r_{ij}) = \sum_{k=1}^{2} A_k (R_k - r_{ij})^3 \Theta (R_k - r_{ij}), \quad R_1 > R_2, \quad (3.16)$$
3.5 Interatomic Potentials

where $a_k$, $r_k$, $A_k$ and $R_k$ are parameters fitted by Ackland et al. [78]. $\Theta(x)$ is the Heaviside step function and

$$\Theta(x) = \begin{cases} 
0 & \text{if } x < 0 \\
1 & \text{if } x > 0
\end{cases} \quad (3.17)$$

The Fe-Fe Interaction

The Fe-Fe interactions are described by a potential with the Finnis-Sinclair form [72], which is smoothly cut-off at 3.62 Å. Finnis and Sinclair adopted the quartic polynomial for the pair potential $V_{ij}$, which is given by

$$V_{ij}(r_{ij}) = \begin{cases} 
(r_{ij} - c)^2 (c_0 + c_1 r_{ij} + c_2 r_{ij}^2) & r_{ij} \leq c \\
0 & r_{ij} > c
\end{cases} \quad (3.18)$$

where $c$ is assumed to lie between the second and third neighbours and the three parameters $c_0$, $c_1$ and $c_2$ are free for fitting experimental data. The expression for the atomic charge density is

$$\phi_{ij}(r_{ij}) = (r_{ij} - d)^2 + \frac{\beta (r_{ij} - d)^3}{d}, \quad (3.19)$$

where $d$ is a parameter having dimension of distance, which is assumed to lie between the second and third neighbours. Thus, $r < d < \sqrt{2}r$, where $r$ is the nearest neighbour spacing. It is important to note that the first neighbours in the bcc structure are at a distance $\sqrt{3}r/2$ and the second are at $r$. In addition, the parameter $\beta$ in Eq. 3.19 was chosen to introduce a maximum in $\phi_{ij}$ within the first-neighbour distance which, for the extreme values of $d$, requires $\beta < 4.975$ if $d = r$ and $\beta < 1.7199$ is $d = \sqrt{2}r$. 

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3.5.2 The Tersoff Potential

Like the embedded atom potentials, Tersoff potentials begin by approximating the binding energy of a system as a sum over sites:

\[ E_b = \sum_i E_i. \]  
(3.20)

However, in this case each site energy is given by an expression that resembles a pair potential. The Si-Si and Si-C interactions in our MD simulations are modelled using the Tersoff potential [79], where the interatomic potential is taken to have the form

\[ E_b = \sum_i E_i = \frac{1}{2} \sum_i \sum_{j(>i)} V_{ij}, \]

\[ V_{ij} = f_C(r_{ij})[a_{ij}f_R(r_{ij}) + b_{ij}f_A(r_{ij})]. \]  
(3.21)

Here the total energy \( E_b \) of the system, is decomposed for convenience into a site energy \( E_i \) and a bond energy \( V_{ij} \). The indices \( i \) and \( j \) run over the atoms of the system, and \( r_{ij} \) is the distance from atom \( i \) to atom \( j \). The function \( b_{ij} \) is the novel feature of this potential, which represents a measure of the bond order, and it is assumed to be a monotonically decreasing function of the coordination of atoms \( i \) and \( j \). The function \( f_R \) represents a repulsive pair potential and \( f_A \) represents the attractive pair potential associated with bonding, and they may be written as

\[ f_R(r) = A \exp(-\lambda_1 r), \]  
(3.22)

and

\[ f_A(r) = -B \exp(-\lambda_2 r), \]  
(3.23)
3.5 Interatomic Potentials

respectively. The extra term $f_C$ is a smooth cutoff function, to limit the range of the potential, since for many applications short-ranged functions permit a tremendous reduction in computational effort. The cutoff function is simply taken as

$$f_C(r) = \begin{cases} 
1, & r < R - D \\
\frac{1}{2} - \frac{1}{2} \sin \left[ \frac{\pi}{2} \frac{(r - R)}{D} \right], & R - D < r < R + D \\
0, & r > R + D,
\end{cases} \quad (3.24)$$

which has continuous value and derivative for all $r$, and goes from 1 to 0 in a small range around $R$. In addition, the function $a_{ij}$ is taken to have the following form:

$$a_{ij} = (1 + \alpha^n \eta_{ij})^{-1/2n}, \quad (3.25)$$

where

$$\eta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}) \exp \left[ \lambda_{ij}^3 (r_{ij} - r_{ik})^3 \right], \quad (3.26)$$

and $\alpha$ is taken sufficiently small such that $a_{ij} \simeq 1$.

The function $b_{ij}$ is given by the following expression:

$$b_{ij} = (1 + \beta^n \zeta_{ij})^{-1/2n}, \quad (3.27)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}) g(\theta_{ijk}) \exp \left[ \lambda_{ij}^3 (r_{ij} - r_{ik})^3 \right], \quad (3.28)$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (h - \cos \theta)^2]^2}, \quad (3.29)$$

where $\theta_{ijk}$ is the bond angle between bonds $ij$ and $jk$, see Fig. 3.2. The parameters $R$, $D$, $\alpha$, $\lambda_i$, $\beta$, $c$, $d$ and $h$ are chosen to model the particular material properties under study.
3.5.3 The Brenner Potential

The interactions between the carbon atoms of the indenter, employed in our simulations, are described by Brenner's many-body potential [80, 81]. This many-body potential was developed to model the intramolecular bonding in hydrocarbon atoms as well as graphite and diamond lattices. The total potential energy is expressed as the sum of all pairwise covalent interactions and each pairwise interaction implicitly contains the many-body information from its immediate surroundings:

\[ E_b = \sum_i \sum_{j(\neq i)} \left[ V_R(r_{ij}) - B_{ij}V_A(r_{ij}) \right], \]  

(3.30)

where \( V_R \) and \( V_A \) are the repulsive and attractive parts of the pairwise interaction and are given by

\[ V_R(r_{ij}) = f_{ij}(r_{ij}) \frac{D_{ij}^e}{S_{ij} - 1} \exp \left[ -\frac{2S_{ij}r_{ij}}{\beta_{ij}} (r - R_{ij}^e) \right], \]  

(3.31)

and

\[ V_A(r_{ij}) = f_{ij}(r_{ij}) \frac{D_{ij}^eS_{ij}}{S_{ij} - 1} \exp \left[ -\frac{2}{S_{ij}} \beta_{ij} (r - R_{ij}^e) \right], \]  

(3.32)

respectively. Moreover, \( r_{ij} \) is the distance between atoms \( i \) and \( j \). The function \( f_{ij}(r) \) explicitly restricts the interaction within the nearest neighbours and is given by

\[ f_{ij}(r) = \begin{cases} 
1, & r < R_{ij}^{(1)} \\
\frac{1}{2} + \frac{1}{2} \cos \left[ \frac{\pi (r - R_{ij}^{(1)})}{R_{ij}^{(2)} - R_{ij}^{(1)}} \right], & R_{ij}^{(1)} < r < R_{ij}^{(2)} \\
0, & r > R_{ij}^{(2)}.
\end{cases} \]  

(3.33)
3.5 Interatomic Potentials

Furthermore, $D_{ij}^r$ is the well depth, $R_{ij}$ is the equilibrium distance, $S_{ij}$ and $eta_{ij}$ are parameters to be fixed depending on the atoms that are interacting (whether C-C, H-H, or C-H). The function $\bar{B}_{ij}$ in Eq. 3.30 is the empirical bond-order function and is given by the average of terms associated with each atom in a bond plus a correction. $\bar{B}_{ij}$ depends on the environment around atom $i$ and $j$, and has a complex mathematical expression given by

$$\bar{B}_{ij} = \frac{(B_{ij} + B_{ji})}{2} + \frac{F_{ij} \left( N_i^{(t)} + N_j^{(t)} + N_{ij}^{\text{conj}} \right)}{2},$$

(3.34)

where $B_{ij}$ is the term that contains second-neighbours effect and the dependence on the bond angles, and it therefore includes the relative position and the coordination number of the particles $i$ and $j$. $F_{ij}$ is a term to correct for the overbinding of radicals and also includes non-local effects to model conjugation. The quantities $N_i^{(t)}$ and $N_j^{(t)}$ are the total number of neighbours \((N_i^{(C)} + N_i^{(H)})\) and \((N_j^{(C)} + N_j^{(H)})\) of atom $i$ and $j$, respectively, $N_{ij}^{\text{conj}}$ depends on whether a bond between carbon atoms $i$ and $j$ is part of a conjugated system.

3.5.4 Empirical Potentials for C-Si-H Systems

For the simulations employing H-terminated Si as substrate a combination [82] of the Brenner potential [80, 81] for C-H systems, the Tersoff potential [79] for Si-C systems and the Si-H potential presented by Murty and Atwater [83] is used to describe the interatomic interactions within the indenter-substrate system. The empirical interatomic potential presented by Murty and Atwater [83] to model the Si-H interactions, is written as

$$V = \frac{1}{2} \sum_{i,j \neq j} \Phi_{ij},$$

(3.35)
where

$$\Phi_{ij} = \left\{ A F_1(N) e^{-\lambda_1 r_{ij}} - B_0 F_2(N) e^{-\lambda_2 r_{ij}} \right\} f_c(r_{ij}) , \quad (3.36)$$

and

$$\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) \left[ c + d \{ H(N) - \cos \theta_{jik} \}^2 \right]$$

$$\times \exp \left[ \alpha \left\{ r_{ij} - R_{ij}^{(e)} \right\}^2 \right] \quad (3.37)$$

The valency of hydrogen is set by the parameters $\alpha$, $\beta$, and $H$ in the many-body part of the potential. Here $F_1$, $F_2$ and $H$ are functions of the coordination $N$ of the $i$th Si atom. To obtain a continuous function for the coordination, we write

$$N_{H}^{i=\text{(Si)}} = \sum_{j=(H)} f_c(r_{ij}) , \quad N_{\text{Si}}^{i=\text{(Si)}} = \sum_{j=(\text{Si})} f_c(r_{ij}) \quad (3.38)$$

and $N = N_{H}^{i=\text{(Si)}} + N_{\text{Si}}^{i=\text{(Si)}}$. The quantities $N_{H}^{i=\text{(Si)}}$ and $N_{\text{Si}}^{i=\text{(Si)}}$ in Eq. 3.38 are the number of silicon atoms bonded to hydrogen and silicon atoms, respectively.

The function $f_c(r_{ij})$ is the cutoff function and is defined as follows:

$$f_c(r_{ij}) = \begin{cases} 
1, & r_{ij} < R - D \\
\frac{1}{2} - \frac{9}{16} \sin \left[ \frac{\pi (r_{ij} - R)}{2D} \right] - \frac{1}{16} \sin \left[ \frac{3\pi (r_{ij} - R)}{2D} \right], & R - D < r_{ij} < R + D \\
0, & r_{ij} > R + D. \quad (3.39) 
\end{cases}$$

The values of $\eta$ and $\delta$ depend only on the atoms $i$ and $j$. The values of $\alpha$, $\beta$, $H(N)$, $c$ and $d$ are those of the potential indicated between atoms $i$ and $k$ in Fig. 3.2.
3.5 Interatomic Potentials

Figure 3.2: Schematic showing some of the terms used in the description of bond order potentials.

3.5.5 The Ziegler-Biersack-Littmark (ZBL) Potential

At very small distances between the nuclei the repulsive interaction can be regarded as essentially Coulombic. At greater distances, the electron clouds screen the nuclei from each other. Thus the repulsive potential can be described by multiplying the Coulombic repulsion between nuclei with a screening function $\phi(r)$,

$$V(r) = \frac{1}{4\pi\varepsilon_0} \frac{Z_1 Z_2}{r} \phi(r), \quad (3.40)$$

where $\phi(r) < 1$ when $r > 0$. Here $Z_1$ and $Z_2$ are the charges of the interacting nuclei, and $r$ the distance between them.

A large number of different repulsive potentials and screening functions have been proposed over the years, some determined semi-empirically, others from theoretical calculations. A much used repulsive potential is the one given by Ziegler, Biersack and Littmark [84], the so-called ZBL repulsive potential. It has been constructed by fitting a universal screening function to theoretically obtained potentials calculated for a large variety of atom pairs. The ZBL screening function has the form

$$\phi(x) = 0.1818e^{-3.2x} + 0.5099e^{-0.9423x} + 0.2802e^{-0.4029} + 0.02817e^{-0.2016x},$$

where $x = r/a_u$ and

$$a_u = \frac{0.8854a_0}{Z_1^{0.23} + Z_2^{0.23}}$$
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($a_0 = 0.529 \text{ Å}$ is the Bohr atomic radius).

In the simulations in this thesis where silver and iron substrates are employed, the interaction between the tip and the substrate atoms, i.e. the Ag-C and Fe-C interactions, are assumed to be purely repulsive and are described by the ZBL potential.

### 3.6 Neighbour Lists

The most computationally expensive procedure during MD simulation is the evaluation of the forces acting upon the atoms in the system. If a short-ranged potential is used to model interactions in the system, only interactions between closely separated atoms are calculated. However, at each stage in the calculation of the potential function, every possible interaction has to be checked to see if atoms are within the interaction distance. So the calculation has a component that scales as $N^2$, where $N$ is the number of atoms in the system.

This checking will quickly swamp the calculations, especially in the case of many-body potentials, where several different interactions between each pair of atoms may be calculated at each timestep. To reduce the amount of checking required a bookkeeping technique known as the neighbour lists are used to keep track of atoms that are interacting, i.e., a list of neighbours within a cutoff distance is created for each atom. Two atoms do not interact if their distance is larger than a certain cutoff distance, $r_c$. Therefore, a considerable saving in computer time is achieved by neglecting pair interactions beyond the cutoff distance. This is done by generating a spherical neighbour list for each atom at the start of the simulation and then only the interaction for those atoms that are found within the cutoff distance from each other is calculated.

Moreover, an update carried out only once every few timesteps can reduce
3.6 Neighbour Lists

Figure 3.3: A schematic representation of a spherical neighbour-list for atom \( a_0 \) in a two-dimensional system. The distances between atom \( a_0 \) and all other atoms are calculated and any atoms within the sphere of radius \( r_c \) are stored. Atoms \( a_1 \) to \( a_9 \) are found within a distance \( r_s \) from atom \( a_0 \) and are included on the neighbour-list. Since atoms \( a_1 \) to \( a_5 \) are within the potential cut-off distance \( r_s \), thus they are the only atoms that contribute to the force acting on atom \( a_0 \). Atoms \( a_6 \) to \( a_9 \) are sited outside the interaction range in the skin radius \( (r_s - r_c) \). Atom \( a_{10} \) lies outside radius \( r_s \) and therefore is not included on the neighbour-list of atom \( a_0 \).

The time taken to update neighbour lists. This is achieved by storing all atoms that are within the cutoff distance, \( r_c \), plus some skin thickness. Therefore, it is only necessary to update neighbour lists if the change in distance between two atoms is greater than this skin thickness. Fig. 3.3 shows a schematic representation of the neighbour-list of atom \( a_0 \), where there is an additional skin to reduce the update frequency. The skin radius is chosen to be of sufficient thickness so that an atom outside the radius \( r_s \), \( i.e., \) atom \( a_{10} \) in Fig. 3.3, cannot displace into the interaction range \( r_c \) after a single integration of the Newton's equations of motion. Therefore, the neighbour lists do not have to be updated every timestep, but only when an atom displaces more than a particular distance, \( (r_s - r_c) \), as shown by Smith [5]. Atoms in the skin can displace to become within the interaction range \( r_c \) without the need for up-
dating the neighbour lists. The choice of the skin thickness is a compromise: larger neighbour lists will need to be reconstructed less frequently, but will not give as much of a saving on CPU time as smaller lists. This choice can easily be made by experimentation: the skin thickness is generally chosen to balance the time computing the surplus atoms on the neighbour list against the time taken to update them.

3.6.1 Concept of Sub-boxes

For larger systems \((N \geq 1000\) or so, depending on the potential range) the generation of neighbour lists itself can be computationally expensive if loops

![Figure 3.4: Two-dimensional representation of the cell index method where the computational box is split into cells. The potential cutoff range is indicated. In searching for neighbours of an atom, it is only necessary to examine the atom's own cell, and its nearest-neighbour cells. For example, the neighbours of the blue atom are to be found in its own cell coloured dark red and its neighbouring cells coloured yellow.](image)

over all atoms are used to determine the atoms within the interaction range
3.7 Parallel Molecular Dynamics

and within the skin radius. Hence, in this case another technique, such as the cell index method [85] becomes preferable. Here the computational (cubic or non-cubic) box with sides of length $L_x \times L_y \times L_z$ is divided into $M_x \times M_y \times M_z$ grid of sub-boxes whose sides is greater than the potential cutoff distance $r_c$. Each cell then has sides of length $l_x \times l_y \times l_z$, where $l_i = L_i/M_i$ and $i = x, y$ or $z$. If there is a separate list of atoms in each of these cells, then searching through the neighbours is a rapid process: it is only necessary to look at atoms in the same cell as the atom of interest, and in nearest neighbour cells. This makes the calculation of the neighbour lists an $O(N)$ operation. A two-dimensional representation of the cell index method is shown in Fig. 3.4. The neighbours of the blue atom in Fig. 3.4 are to be found in its own cell coloured dark red and in its neighbouring yellow-coloured cells.

3.7 Parallel Molecular Dynamics

Computationally, MD simulations are “large” in two domains: the number of atoms and number of timesteps. Since the length scale for atomic coordinates is Ångstroms then in three dimensions many millions of atoms must usually be simulated to approach even the sub-micron scale. In addition, in liquids and solids the timestep size is constrained by the demand that the vibrational motion of the atoms be accurately tracked. This limits timesteps to the femtosecond scale and so tens or hundreds of thousands of timesteps are necessary to simulate even picoseconds of time. These are the two main reasons that explain why MD is computationally expensive. Researchers in the field have typically focussed their efforts on simplifying models and identifying what may be neglected while still obtaining acceptable results. This has led to some scepticism on the ability of MD to be used as a predictive tool for experimental work. Parallel computers hold the key to making relevant
calculations tractable without compromise.

In recent years, there has been considerable interest in devising parallel MD algorithms. The natural parallelism in MD is that the force calculations and velocity/position updates can be done simultaneously for all atoms. In this section three parallel algorithms (atom-decomposition, force-decomposition and spatial-decomposition algorithms) for classical molecular dynamics are introduced. For more information on these algorithms the reader is referred to Ref. [86] by Plimpton. These parallel algorithms are suitable for a general class of MD problems where the forces are limited in range, i.e. each atom interacts only with other atoms that are geometrically nearby. Solids and liquids are often modelled this way when the interatomic bonding is covalent or metallic. The objective in each of these algorithms is to divide the force computations in Eq. 3.1 evenly across the processors so as to extract maximum parallelism. The simulations in this thesis were performed using parallel MD with the following two different decomposition methods: atom decomposition (AD) and spatial decomposition (SD).

### 3.7.1 Atom-Decomposition (AD) Algorithm

In this approach, a pre-determined set of force computations is assigned to each processor. This particular assignment remains fixed for the duration of the simulation. Hence, each of the, say $P$, processors is assigned a group of $N/P$ atoms at the beginning of the simulation, where $N$ is the total number of atoms in the system. This method is called an atom decomposition (AD) of the workload. Atoms in a group need not have any special spatial relationship to each other. Thus, a processor will compute forces on only its $N/P$ atoms and will update their positions and velocities for the duration of the simulation, no matter where they move in the physical domain. For example, the first $N/P$ atoms are assigned to the first processor, the second $N/P$ atoms to the second
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processor and so on. An example is illustrated in Fig. 3.5, for 20 atoms and 4 processors. In this figure, the first processor calculates the dynamics of the blue atoms, the second processor calculates the dynamics of the red atoms, the third processor the green atoms and the fourth processor the black atoms. Each processor calculates the force and updates the velocities and positions of only the \( N/P \) atoms which are assigned to them. This is done irrespective of where the atoms move in the physical domain. In order to calculate the force for the \( N/P \) atoms each processor needs to know the coordinates of all \( N \) atoms. Hence, at every timestep each processor must receive updated atom positions from all the other processors and this operation is called all-to-all communication (this all-to-all communication procedure is termed an expand operation). For this purpose, lists of the coordinates for all the \( N \) atoms need
to be constructed by each processor.

The computational work involved in the algorithm is the $N \times N$ force matrix $F$. The $(ij)$ element of $F$ represents the force on atom $i$ due to atom $j$. The matrix $F$ is skew-symmetric, i.e. $F_{ij} = -F_{ji}$, due to Newton’s third law.

Now, there are two types of any parallel algorithm. The first group does not use Newton’s third law, whereas the second group take Newton’s third law of motion into consideration. In a sequential MD program it is easy to use Newton’s third law. However, in a parallel program it is more complicated since the $N$ atoms are partitioned and assigned to different processors. Therefore, if different processors own atoms $i$ and $j$ as is usually the case, both processors compute the $(ij)$ interaction and store the resulting force on their atom. We shall now discuss both cases for the atom-decomposition algorithm only, and hence for an insight into how it is implemented for the other two parallel algorithms (force-decomposition and spatial-decomposition discussed in Sections 3.7.2 and 3.7.3, respectively) the reader is referred to Ref. [86] by Plimpton.

**Atom-decomposition without using Newton’s third law (AD1)**

Fig. 3.6 shows the main steps in this method. The first step involve the calculation, by each processor, of the new coordinates for its $N/P$ atoms. Since each processor needs information about the coordinates of all the $N$ atoms for the list construction, thus it is compulsory for every processor to expand all the coordinates of its $N/P$ atoms to the rest of the processors. Consequently, each processor will hold information on all the $N$ atoms in the system and will construct full list of atoms situated in every sub-box. This, in turn, enable each processor to calculate the force and velocities for its $N/P$ atoms.
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Atom-decomposition using Newton’s third law (AD2)

The atom-decomposition algorithm AD1 does not consider Newton’s third law and so if different processors own, say atoms $i$ and $j$, both processors compute the interaction between the two atoms and the resulting force $F_{ij}$ is stored in one processor and $F_{ji}$ is stored in the other processor. It is difficult to do otherwise for many-body interactions since it would require the splitting of the calculation of any summation term among the processors involved. But for pair interactions there was no need to calculate $F_{ji}$ since $F_{ji}$ could have been deduced from $F_{ij} = -F_{ji}$ (by Newton’s third law). This can be avoided by using a modified force matrix $G$, which references each pairwise interaction.

![Figure 3.6](image)

Figure 3.6: Figure showing the main steps involved in the atom-decomposition algorithm AD1.
only once. The matrix $G$ is built up as follows:

$$ G_{ij} = \begin{cases} 
F_{ij}, & i > j \text{ and } (i + j) \text{ is even} \\
0, & i < j \text{ and } (i + j) \text{ is odd} 
\end{cases} $$ (3.41)

Figure 3.7: Figure showing the main steps involved in the atom-decomposition algorithm AD2.
A modified atom-decomposition algorithm AD2 that uses $G$ to take advantage of Newton's third law is outlined in Fig. 3.7. The first three steps of this algorithm are similar to those in the atom-decomposition algorithm AD1. But the fourth step is slightly different. Here, both the distance and the force between the atoms are calculated only once, and only half as many neighbour list entries are made by each processor since $G$ has only half the non-zero entries of $F$. If a processor does not calculate the complete force for its atoms, this implies that that processor needs to exchange data from the processor that has got the information on that force. When each processor calculates the force between atoms $i$ and $j$, it should save it in vector $F$ for its own atoms (assigned to it) and in a vector $G$ for data exchange. For example, if processor 1 calculates the force for the third atom and it has vector $F[1 \ldots N]$ and vector $G[1 \ldots N]$, then the elements $F[3]$ and $G[3]$ store the force for the atom number 3. The force in vector $G$ is shared to all the other $(P - 1)$ processors.

The atom-decomposition of the parallel MD code employed to do the simulations in this thesis is done using the AD2 algorithm, which takes advantage of Newton's third law. For a more detailed description on the atom-decomposition of the parallel MD code employed, the reader is referred to the thesis of David Christopher [87].

### 3.7.2 Force-Decomposition (FD) Algorithm

The second parallel MD algorithm is the force-decomposition (FD) algorithm and is based on a block-decomposition of the force matrix rather than a row-wise decomposition as used in the atom-decomposition algorithm, *i.e.* the force matrix is divided between processors. Hence, each processor calculates the forces that belong to a part of the matrix. To reduce communication the block-decomposition of a permuted force matrix $F'$ is done instead, which is
Figure 3.8: Figures illustrating the decomposition of the permuted force matrix $F'$ for (a) 8 and (b) 16 processors. The numbers in blue denote the number associated to each of the processor. The force $F_{ij}$ is the force on atom $i$ due to atom $j$. The red line shows the partition between the processors. The sum of the forces $(F_{i1} + F_{i2} + \cdots + F_{iN})$ is the total force on atom $i$ due to the remaining $(N - 1)$ atoms in the system.
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formed by rearranging the columns of $F$ in a particular way. Figs. 3.8(a) and 3.8(b) illustrate how the permuted force matrix $F'$ is divided between 8 and 16 processors, respectively.

Let $N_{\text{row}}$ and $N_{\text{column}}$ denote the number of rows and columns in the permuted force matrix, respectively, then $N_{\text{row}} \times N_{\text{column}} = P$, where, as usual, $P$ is the number of processors. Moreover, the length of a row and column in a particular sub-block (for example, in the shaded part in Fig. 3.8(b)) of the permuted force matrix will be given by $N/N_{\text{row}}$ and $N/N_{\text{column}}$, respectively. Now, if $P = x^2$, where $x$ is any integer, (e.g. $P = 4, 9, 16, 25, \ldots$) then the number of rows will be equal to the number of columns, and subsequently, the length of any particular row will be equal to the length of any particular column. In that case, the length of any row or column of a sub-block of the force matrix will be given by $N/\sqrt{P}$, since $N_{\text{row}} = N_{\text{column}}$ and $N_{\text{row}} \times N_{\text{column}} = P$, therefore implying that $N_{\text{row}} = N_{\text{column}} = \sqrt{P}$. Hence, the sub-block $F_z'$ (where $z = 1, \ldots, P - 1$) owned by processor $P_z$ will be of size $\left(\frac{N}{\sqrt{P}}\right) \times \left(\frac{N}{\sqrt{P}}\right)$. Processor $P_z$ owns and will update the $N/P$ atoms, whose positions are stored in the sub-vector $x_z$.

To explain the force-decomposition algorithm let us consider a simple example where $N = 8$ and $P = 4$. The elements of the vector $X$ are the position vectors of the eight atoms and $X$ is given by

$$X = \begin{bmatrix} x_1, x_2, x_3, x_4, x_5, x_6, x_7, x_8 \end{bmatrix},$$

where $x_i$ ($i = 1, \ldots, 8$) is the position vector of atom $i$. Now allocating the 8 atoms to the 4 processors, the position vector $X$ takes the form as shown in Fig. 3.9(a), where the $x_z$ ($z = 0, P - 1$ and for our example $z = 0, 3$) pieces are ordered in row-order and $x_z$ is the portion allocated to processor $P_z$. The permuted position vector $X'$ is given by the expression in Fig. 3.9(b), where the $x_z$ pieces are ordered in column-order. Thus, in the 16-processor example
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\[ \mathbf{X} = \begin{bmatrix} x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 & x_8 \\ x_0 & x_1 & x_2 & x_3 \end{bmatrix} \]

(a)

\[ \mathbf{X'} = \begin{bmatrix} x_1 & x_2 & x_5 & x_6 & x_3 & x_4 & x_7 & x_8 \\ x_0' & x_1' & x_2' & x_3' \end{bmatrix} \]

(b)

Figure 3.9: (a) The position vector \( \mathbf{X} \), where \( x_0 = [x_1, x_2] \) is allocated to processor \( P_0 \), \( x_1 = [x_3, x_4] \) to processor \( P_1 \), \( x_2 = [x_5, x_6] \) to processor \( P_2 \), and \( x_3 = [x_7, x_8] \) to processor \( P_3 \). (b) The permuted position vector \( \mathbf{X'} \), where the \( x_z \) (\( z = 0, 1, 2, 3 \)) pieces are ordered in column-order.

Figure 3.10: Figure illustrating the decomposition of the permuted force matrix \( \mathbf{F'} \) for the case where \( P = 4 \) and the total number of atoms is \( N = 8 \). The subscripts of the matrix elements are written in different colours to accentuate the difference between the permuted force matrix \( \mathbf{F'} \) and the original force matrix \( \mathbf{F} \).
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shown in Fig. 3.8(b), $X$ stores each processor's piece in the usual order (0, 1, 2, 3, 4, 5, ..., 14, 15) whereas $X'$ stores them as (0, 4, 8, 12, 1, 5, 9, 13, 2, 6, 10, 14, 3, 7, 11, 15).

The columns of $F'$ is spanned by the permuted position vector $X'$. Thus, the permuted force matrix $F'$ is formed by re-arranging the columns of the force matrix $F$. For our example where $N = 8$ and $P = 4$, $F'$ takes the form as shown in Fig. 3.10. Hence the element $F'_{ij}$ is the force on atom $i$ in vector $X$ due to atom $j$ in the permuted vector $X'$.

To compute the matrix elements in the sub-block $F'_z$, which is of size \( \left( N/\sqrt{P} \right) \times \left( N/\sqrt{P} \right) \), processor $P_z$ must know one $N/\sqrt{P}$-length piece of each of the $X$ and $X'$ vectors, which are denoted as $x_\alpha$ and $x'_\beta$, respectively (refer to Fig. 3.10). Both the subscripts $\alpha$ and $\beta$ run from 0 to $\sqrt{P} - 1$, and that $x_\alpha \subset x \subset X$ and $x'_\beta \subset x'_z \subset X'$. In our example $\alpha = \beta = 0, 1$ and

\[
x_0 = \begin{bmatrix} x_1, x_2, x_3, x_4 \end{bmatrix} \quad x_1 = \begin{bmatrix} x_5, x_6, x_7, x_8 \end{bmatrix}
\]

and

\[
x'_0 = \begin{bmatrix} x_1, x_2, x_5, x_6 \end{bmatrix} \quad x'_1 = \begin{bmatrix} x_3, x_4, x_7, x_8 \end{bmatrix}
\]

The matrix elements of $F'_z$ are computed and stored into corresponding force sub-vectors $f_\alpha$ and $f'_\beta$. Thus, for processor 5 in Fig. 3.8(b), $x_\alpha$ consists of the $x$ sub-vectors (4, 5, 6, 7) and $x'_\beta$ consists of the $x'$ sub-vectors (1, 5, 9, 13).

Each processor has updated copies of the required atom positions $x_\alpha$ and $x'_\beta$ at the beginning of the timestep. Then neighbour-lists are constructed, which are then used to compute the matrix elements of the sub-block $F'_z$. As the elements are computed they are summed into a local copy of $f_\alpha$. A fold operation is performed within each row of processors so that processor $P_z$ obtains the total forces on its $N/P$ atoms. The fold operation in this algorithm is different since $f_\alpha$ being folded is only of length $N/\sqrt{P}$ and only the $\sqrt{P}$
processors in one row participates in the fold operation. Hence, this operation scales as \( N/\sqrt{P} \) instead of \( N \) compared to atom-decomposition algorithm.

Processor \( P_z \) then uses the total forces to update its \( N/P \) atom positions in \( x_z \). These updated positions are then shared with all the processors that will need them for the next time step and these processors are the processors which share a row or column with processor \( P_z \). Using the permuted matrix \( F' \) saves extra communication with this step. The permuted form of \( F' \) causes \( x_z \) to be a component of both \( x_{\alpha} \) and \( x'_{\beta} \) for each \( P_z \), which would not have been the case if we had block-decomposed the original force matrix \( F \).

### 3.7.3 Spatial-Decomposition (SD) Algorithm

The third parallel MD algorithm is the spatial-decomposition (SD) algorithm and is the most complex of the parallel algorithms. Here the physical simulation domain is subdivided into small 3D boxes, one for each processor, and so each processor is assigned a portion of the physical domain. Each processor computes forces and updates the positions and velocities of all atoms within its box at each timestep. As the simulation progresses, processors exchange atoms, i.e. atoms are re-assigned to new processors as they move through the physical domain. Each processor in the SD algorithm maintains two data structures, one for the \( N/P \) atoms in its box and one for atoms in nearby boxes. In the first data structure, each processor stores complete information – positions, velocities, neighbour lists, and so on. This data is stored in a linked list to allow insertions and deletions as atoms move to new boxes. In the second data structure only atom positions are stored. Communication between the processors at each timestep keeps this information current. The communication required in SD is thus local in nature as compared to global
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Figure 3.11: Figure illustrating the spatial-decomposition algorithm for the case of 9 processors, where the physical simulation domain is subdivided into small boxes and each portion of the physical domain is allocated to each processor. The area coloured in red illustrates the atom positions that processor 4 needs to know from the neighbouring processors in order to perform its calculations.

In this algorithm each processor performs calculations for only a part of all the space, which means that the number of atoms is not necessarily the same for each processor. Each processor has two types of atoms: atoms which it calculates, and atoms whose coordinates it needs for the force calculation of the first group of atoms. Fig. 3.11 illustrates this for the 2-D case. Here, the space is divided into parts and each processor has a boundary area. Atoms situated in this area are necessary for the calculation of the forces for all the other processors. This means that each processor needs the coordinates from the neighbouring processors, and should send the coordinates of their own atoms to the other processors. This is the main principle of spatial-decomposition method.
3.8 Comparison of the parallel algorithms

Each of the three parallel algorithms discussed above has advantages and disadvantages. The atom-decomposition algorithm is simplest to implement and the load balance is done automatically. One main disadvantage of the atom-decomposition algorithm is that the communication costs start to dominate the run time on large numbers of processors and this can be explained by the fact that the AD algorithm performs all-to-all communication. Thus, if the communication cost is expected to be negligible then the AD algorithm is favourable since simplicity outweighs the inefficient communications. Typically this will only be true for small $P$.

On the other hand, the force-decomposition algorithm is also relatively simple, despite the fact that it often requires some pre-processing to assure load balance. The parallel efficiency of both the AD and the FD algorithms is independent of $N$. Once the number of processors is large enough such that the FD algorithm is noticeably faster than the AD algorithm, it will remain faster as the number of processors increases. For the benchmark problem tested by Plimpton [86], the AD algorithm was found to be favourable for $P \leq 16$.

Any form of short-range interatomic forces function can be implemented within the AD and SD framework. However, the FD algorithm is less general in this respect. For example, if higher-order (3-body, 4-body, and so) interactions are included in the force model, we have to make sure that the processors knows sufficient information to compute any given interaction.

The SD algorithm is the best algorithm when large numbers of processors are employed. The crossover to using this algorithm is not always easy to understand because for a fixed $P$, the scaling for the SD algorithm is not linear, i.e. the parallel efficiency is dependent on $N$. This is explained by the fact that each processor's box has a volume of $d^3 = N/P$, where $d$ is the box length, but it computes and communicates information in an extended
volume of \((d + r_s)^3\), where \(r_s\) is the neighbour-list cut-off distance. For small \(N\) the communication costs are significant and the efficiency is poor, whereas for large \(N\) the efficiency is optimal. However, the SD algorithm suffers more easily from load imbalance and is more difficult to implement efficiently. But, as \(N\) increases for a fixed \(P\) there will be a crossover point when comparing the SD algorithm with the FD algorithm. And this point is where the SD algorithm becomes faster. The crossover point is actually a function of the complexity of the model, the cut-off distance, and the computational and communication capabilities of a particular parallel machine. It will also be a function of \(P\), especially the case where the number of processors is large as the communication is always local in the SD algorithm.

The simulations in this thesis were performed using the AD and SD algorithms. The AD algorithm was initially employed due to its simplicity to implement compared to the FD and SD algorithm and also because we had access to a limited number of processors. We then employed the SD algorithm, because it allowed us to study bigger system sizes since we had access to a larger number of processors. We have not utilised the FD algorithm in this thesis due to the fact it is very complicated to implement when using many-body potentials, such as in our case.

### 3.9 MPI - Message Passing Interface

The main concept in parallel computing is message passing, which can be described as the method by which data from one processor's memory is copied to the memory of another processor. In distributed memory systems, data is generally sent as packets of information over a network from one processor to another. A message may consist of one or more packets, and usually includes routing and other control information. Fig. 3.12 show an example of the
distributed memory system with three processors A, B and C. Every processor has its own local memory which can be accessed directly only by its own CPU, and transfer of data from one processor to another is performed over a network. The distributed memory system differs from the shared memory system, which permit multiple processors to directly access the same memory resource. A process is a set of executable instructions (program) running on a processor and one or more processes may execute on a processor. In a message passing system, all processes communicate with each other by sending messages - even if they are running on the same processor. However, for reasons of efficiency, message passing systems generally associate only one process per processor.

The Message Passing Interface (MPI) is a set of functions enabling programmers to write high-performance parallel programs that pass messages between serial processes to make up an overall parallel job. MPI is the culmination of decades of research in parallel computing and the goal of the MPI is to establish a practical, portable, efficient, and flexible standard for message passing. The two main reasons for using MPI are standardisation and
portability. MPI is the only message passing library which can be considered as standard and it is supported on virtually all high-performance computing platforms. MPI is also portable and thus, there is no need to modify the source code when an application is ported to a different platform that supports MPI.

LAM is a simple yet powerful environment for running and monitoring MPI applications on clusters. LAM takes care of the parallel coordination and provides high performance on a variety of platforms. An example of a high-quality open-source implementation of the MPI specification is the LAM/MPI [88]. Another example of a freely available and portable implementation of MPI is MPICH [89].
Chapter 4

Crystal Structures and Defects

4.1 Introduction

In this chapter, a brief introduction is given to the crystal structure of the materials considered in our investigation of friction at the atomic-scale. We know that the behaviour of electrons determine the way the atoms interact, i.e., the type of bonding (metallic, ionic, covalent, and Van der Waals) that holds the atoms in a solid together. But the knowledge of crystal structure and bonding is not sufficient to predict the physical properties of materials. Thus, we have extended our discussion to the different types of imperfections or defects in the ideal arrangement of atoms in a crystal. This will enable us to see that the presence of a relatively small number of defects can have a profound impact on the physical properties of materials, the control (and intentional introduction) of defects is important in many kinds of material processing. This discussion on defects in crystals will also be helpful in understanding some of the later chapters in this thesis. In this thesis, we will concentrate more on the generation of line defects called dislocations and the discussion will be restricted to dislocations in systems with face-centred cubic (fcc), body-centred cubic (bcc) and diamond crystal structures. For a more detailed discussion on
the vast subject of dislocations in different crystal structures (for example, the
close-packed hexagonal structures), the reader is referred to Hull and Bacon
[90].

4.2 Crystal Structures

Metals and many important classes of non-metallic solids are crystalline, i.e.,
the constituent atoms are arranged in a pattern that repeats itself periodically
in three dimensions. The actual arrangement of the atoms is described by
the crystal structure. These arrangements have a direct effect on the physical
properties of the material and they commonly take the form of cubes, rectan-
gular solids, hexagonal solids and so on. The crystal structures of most pure
metals are simple, the three most common structures being the face-centred
cubic (fcc), the body-centred cubic (bcc) and the hexagonal close-packed (hcp)
structures.

4.2.1 Face-centred cubic Structure

Many of the technologically important metals possess the fcc structure, for ex-
ample, the catalytically important precious metals (platinum, rhodium, pal-
ladium) all exhibit an fcc structure. In our investigation of friction on the
atomic-scale we have studied silver (Ag), which has an fcc crystal structure.
The fcc crystal structure can be described as a stack of atom layers in which
the arrangement of atoms in each layer is identical. The sequence of the atom
layers in the stack, i.e., the stacking sequence, is referred to by fixing one layer
as an A layer and all other layers with atoms in identical positions as A layers
also. Layers of atoms in other positions in the stack are referred to as B, C,
D layers, and so on. Fig. 4.1(a) shows a unit cell of the fcc crystal structure,
where the atoms are situated at the corners of the unit cell and at the centres
of all the cube faces and a material with an fcc structure can be regarded as an almost endless repetition of this unit cell. The lattice parameter of a crystalline material with an fcc structure is given by \( a_0 = \sqrt{2}r \), where \( r \) is the nearest neighbour spacing. The stacking sequence of the \{100\} and \{110\} planes is \( AB\ AB\ AB.\ldots \), and the stacking sequence of the \{111\} planes is \( ABC\ ABC\ ABC\ldots \), which is illustrated in Fig. 4.1(b). The atoms in the \{111\} planes are in the most close-packed arrangement possible for spheres.

### 4.2.2 Body-centred cubic Structure

The body-centred cubic unit cell is cubic (all sides of the same length and all face perpendicular to each other) with an atom at each corner of the unit cell and an atom in the centre of the unit cell, as shown in Fig. 4.2(a). The unit cell completely describes the structure of a solid with a bcc structure, which can be regarded as an almost endless repetition of the unit cell. The lattice parameter is given by \( a_0 = \sqrt{3}r/2 \) and the spacing of atoms along the \langle 110 \rangle directions is \( \sqrt{2}a_0 \). The stacking sequence of \{100\} and \{110\} planes is \( AB\ AB\ AB\ldots \), as shown in Fig. 4.2(b). In this thesis, one of the materials considered with a bcc structure is iron (Fe).
4.2 Crystal Structures

Figure 4.2: (a) Schematic representation of the unit cell and (b) the plan view showing the arrangement of atoms in the (110) surface, of the body-centred cubic crystal structure.

4.2.3 Diamond Crystal Structure

The diamond crystal structure is very common in semiconductor materials, for example, silicon and germanium. The diamond lattice is composed of two interpenetrating fcc lattices, one displaced 1/4 of a lattice constant in each cartesian direction from the other. Each site is tetrahedrally coordinated with four other sites in the other sublattice, as shown in Fig. 4.3. The difference between the fcc lattice structure and the diamond lattice structure can be

Figure 4.3: Schematic representation of the diamond-cubic unit cell.

thought of as an extra four atoms (refer to the dark circles in Fig. 4.3) in the fcc unit cell. Diamond, silicon and germanium are examples of materials with
the diamond crystal structure. The cubic structure of diamond, silicon and germanium is one of the simplest and most widely studied. The covalent bond formed by two atoms sharing electrons is strongly localised and directional, and this feature is important in determining the characteristics of dislocations. Dislocations in these semiconductors affect both the mechanical and the electrical properties.

The close-packed \{111\} planes in the diamond crystal structure have six-fold stacking sequence $AaBbCcAaBb\ldots$ as shown in Fig. 4.4. Atoms of adjacent layers of the same letter such as $Aa$ lie directly over each other.

Dislocations produced in materials with the diamond crystal structure belong to either the glide set or the shuffle set, as indicated in Fig. 4.4, which we shall discuss in more details later on in Section 4.3.4.

4.3 Defects in Crystal Structures

All the atoms in a perfect lattice are at specific sites (ignoring thermal vibrations). But a perfect crystal with regular arrangement of atoms rarely exist in reality. Almost all real crystals contain imperfections which may be point, line,
4.3 Defects in Crystal Structures

surface or volume defects, and which disturb locally the regular arrangement of the atoms. The presence of these defects within the structures of crystalline solids can significantly modify the properties of these crystalline solids. In this chapter, we will focus mainly on point and line defects.

4.3.1 Point defects: Vacancies and Interstitials

Point defects are the most common defects. In a pure metal two types of point defects are possible, namely vacancies, and interstitials. These intrinsic defects are illustrated in Fig. 4.5.

Figure 4.5: Schematic representation of different point defects in a crystal: (1) vacancy; (2) self-interstitial; (3) interstitial impurity; (4) and (5) are substitutional impurities. The red arrows show the local stresses introduced by the point defects.

At high temperatures atoms frequently and randomly change their posi-
tions leaving behind empty lattice sites, called vacancies. The higher the temperature, the more often atoms jump from one equilibrium position to another and as a result larger number of vacancies can be found in a crystal. In fact the number of vacancies, \( N_v \), increases exponentially with the absolute temperature, \( T \), and can be estimated using the following equation (Boltzmann Distribution):

\[
N_v = N_{rs} \exp \left( \frac{-E_v}{k_B T} \right),
\]

where \( N_{rs} \) is the number of regular lattice sites, \( k_B \) is the Boltzmann constant, and \( E_v \) is the energy needed to form a vacant lattice site in a perfect crystal.

On the other hand, interstitials are atoms that are squeezed in between regular lattice sites. If the interstitial atom is of the same species as the lattice atoms, it is called a self-interstitial. Creation of a self-interstitial causes substantial distortions in the surrounding lattice and costs more energy as compared to the energy for creation of a vacancy \((E_i > E_v)\) and, under equilibrium conditions, self-interstitials are present in lower concentrations than vacancies. Foreign, usually smaller atoms (e.g., carbon, nitrogen, hydrogen, oxygen), that sit in between lattice sites are called interstitial impurities. They introduce less distortion to the lattice and are more common in real materials and more mobile. If the foreign atom replaces or substitutes a matrix atom, it is called a substitutional impurity.

### 4.3.2 Line defects: Dislocations

Dislocations are line defects and there are two basic types of dislocations: edge dislocations and screw dislocations. Edge dislocations are dislocations whose Burgers vector (discussed in Section 4.3.4) is directly perpendicular to the dislocation, whereas screw dislocations are parallel to the direction in which the crystal is being displaced (i.e., Burgers vector is parallel to the
4.3 Defects in Crystal Structures

dislocation line). Edge and screw dislocations are extreme forms of the possible dislocation structures and they usually split into “partial” dislocations. An edge dislocation can be regarded as the insertion of an extra half plane of atoms into a perfect lattice, as shown in Fig. 4.6(a), where the extra half plane is encircled. On the other hand, the arrangement of atoms round a screw dislocation can be simulated by displacing part of the crystal on one side, refer to Fig. 4.6(b).

![Figure 4.6: Schematic representation of (a) an edge dislocation, and (b) a screw dislocation. (From Surface Effects in Adhesion, Friction, Wear, and Lubrication, D. H. Buckley (1981), Pg. 157).](image)

Dislocations move along the most dense planes in the most dense directions, this is because the stress needed to move the dislocation increases with the length of the Burgers vector and with the spacing between the planes. There are many such dense planes in fcc and bcc metals, and hence these materials have high ductility, i.e., they deform a great deal before they break.

Line defects can serve as sites for generating weak regions in the material where cracks and voids can develop along with wear particles. For example, the intersection of dislocations along slip lines can produce voids, these voids can grow with progressive deformation until in weakened subsurface regions a
crack can be initiated. The crack can then subsequently work its way to the surface and generate a wear particle [62].

4.3.3 Stacking Faults

Perfect lattices can be described as a stack of identical atom layers arranged in a regular sequence. A stacking fault is a planar defect and it is a local region in the crystal where the regular sequence has been interrupted. Stacking faults are not expected in planes with \(AB\ AB\ AB\ldots\) sequences in bcc or fcc lattices because there is no alternative site for an \(A\) layer resting on a \(B\) layer. However, for \(ABC\ ABC\ ABC\ldots\) stacking of the close-packed planes there are two possible positions of one layer resting on another: a close-packed layer of atoms resting on an \(A\) layer can rest equally well in either a \(B\) or a \(C\) position. In an fcc lattice two types of stacking fault are possible and they are referred to as intrinsic and extrinsic. These are described by considering the change in sequence resulting from the removal or introduction of an extra layer. Fig. 4.7(a) shows an intrinsic fault, where part of a \(C\) layer has been removed which results in a break in the stacking sequence. In Fig. 4.7(b) an

![Diagram of stacking faults](image)

Figure 4.7: Figures showing stacking faults in a face-centred cubic lattice. The normal stacking sequence of (111) planes is denoted by \(ABC\ A\ldots\) Planes in normal relation to one another are separated by \(\triangle\), whereas those with a stacking error by: (a) intrinsic stacking fault, (b) extrinsic stacking fault. (From Introduction to Dislocations, D. Hull and D. J. Bacon (1984), Pg. 13).
extra $A$ layer has been introduced between a $B$ and a $C$ layer. Thus, here there are two breaks in the stacking sequence and it is referred to as an extrinsic fault.

As mentioned in Section 4.2.3, the stacking sequence of the the close-packed \{111\} planes in the diamond crystal structure is $AaBbCcAaBb\ldots$ (see Fig. 4.4). Atoms of adjacent layers of the same letter such as $Aa$ lie directly over each other. Insertion or removal of such pairs usually gives rise to planar stacking faults, but this does not change the tetrahedral bonding in materials with diamond crystal structure. By reference to the face-centred cubic metals, the intrinsic fault has stacking sequence $AaBbAaBbCc\ldots$ and the extrinsic fault has $AaBbAaCcAaBb\ldots$. Faults formed between adjacent layers of the same letter do not restore tetrahedral bonding and have a high energy.

### 4.3.4 Burgers Vector and Burgers Circuit

The most practical definition of a dislocation is given in terms of the Burgers circuit, which is any atom-to-atom path taken in a crystal containing dislocations which forms a closed loop. Such a path is represented in Fig. 4.8(a), i.e., MNOPQ. If the same atom-to-atom step sequence is made in a dislocation-free crystal and the circuit does not close, then the first circuit, Fig. 4.8(a), must enclose one or more dislocations. The vector required to complete the circuit is called the Burgers vector, $b$. It is essential that the circuit in the real crystal passes entirely through "good" parts of the crystal.

**Face-centred cubic structures**

Many common metals such as copper, silver, gold, aluminium, nickel and their alloys, have a fcc structure. The shortest lattice vectors, and therefore the most likely Burgers vectors for dislocations in the fcc crystal structure, are of the type $\frac{1}{2}(110)$ and $\langle001\rangle$. The energy of a dislocation is proportional to the square
Figure 4.8: (a) Burgers circuit round an edge dislocation, (b) the same circuit in a perfect crystal; the closure failure is the Burgers vector. (From Introduction to Dislocations, D. Hull and D. J. Bacon (1984), Pg. 19).

of the magnitude of its Burgers vector, $|b|^2$ ([90], section 4.4). Therefore, the energy of $\frac{1}{2}(110)$ dislocations will be only half that of $\langle 001 \rangle$, i.e., $a_0^2/2$ compared with $a_0^2$, where $a_0$ is the lattice parameter of the respective material under consideration. Thus, $\langle 001 \rangle$ dislocations are much less favoured energetically. In fact, $\langle 001 \rangle$ dislocations have not been observed in fcc structures. Since $\frac{1}{2}(110)$ is a translation vector for the face-centred cubic lattice, glide of a dislocation with this Burgers vector leaves behind a perfect crystal and the dislocation is a perfect dislocation.

On the other hand, the motion of a dislocation whose Burgers vector is not a lattice vector leaves behind an imperfect crystal containing a stacking fault. Thus, when a stacking fault ends inside a crystal, the boundary in the plane of the fault, separating the faulted region from the perfect region of the crystal is a partial dislocation. Two of the important partial dislocations, recognised
4.3 Defects in Crystal Structures

in face-centred cubic metals, are the Shockley partial, which is associated with slip, and the Frank partial. Fig. 4.9 illustrates the formation of a Shockley partial edge dislocation. At the right of the diagram the A layers rest on the C layers and the lattice is perfect. At the left of the diagram in Fig. 4.9 the A layers along LM have slipped in a [121] direction to a B layer position, and have produced a stacking fault and a partial dislocation. The slip vector, which is in the slip plane, is \( \mathbf{b} = \frac{1}{6} [121] \), and the magnitude of the vector is \( a_0/\sqrt{6} \).

Body-centred cubic structures

The shortest lattice vector, \( \text{i.e.,} \) the Burgers vector of the perfect slip dislocation in body-centred cubic metals (e.g. iron, chromium, tungsten, sodium and potassium) is of the type \( \frac{1}{2} \langle 111 \rangle \). It is a feature of bcc metals that stacking faults have not been observed experimentally, and it has been confirmed through computer models that stable faults are unlikely to exist in the bcc...
structure [90].

**Diamond crystal structures**

In diamond cubic structures perfect dislocations have Burgers’ vector $\frac{1}{2}(110)$. The perfect dislocation dissociates into two $\frac{1}{6}(112)$ Shockley partials separated by the intrinsic stacking fault, as in the fcc metals.

As mentioned earlier, dislocations produced in materials with the diamond crystal structure belong to either the glide set or the shuffle set. Dislocations of both sets can dissociate, but the mechanism of dissociation is different for the two cases. In the glide set, the perfect dislocation dissociates into two $\frac{1}{6}(112)$ Shockley partials separated by the intrinsic stacking fault, as in the face-centred cubic metals. Dissociation of the shuffle dislocation is not so simple and it occurs by the nucleation and glide of a Shockley partial of the glide type between an adjacent pair of $\{111\}$ layers. This results in a fault of the glide set bounded on one side by a Shockley partial and on the other by a Shockley partial and, depending on whether the glide fault is above or below the shuffle plane, a row of interstitials or vacancies.

### 4.3.5 Slip

There are two basic types of dislocation movement, glide or conservative motion and climb or non-conservative motion. Glide of many dislocations results in slip, which is the most common manifestation of plastic deformation in crystalline solids. Slip results in the formation of steps on the surface of the crystal and it can be conceived as the sliding or the successive displacement of one plane of atoms over another on so-called *slip planes*. The slip plane is normally the plane with the highest density of atoms and the direction of slip is the direction in the slip plane in which the atoms are most closely spaced. Thus, in face-centred cubic metals, slip often occurs on the $\{111\}$ planes in
4.3 Defects in Crystal Structures

the (110) directions and gliding in any other planes occurs very rarely. On the other hand, in body-centred cubic metals the slip direction is the (111) close-packed direction, but the slip plane is not well defined on a macroscopic scale. Microscopic evidence suggests that slip in body-centred cubic metals occurs also on the \{112\} and \{110\} planes and that \{110\} slip is preferred at low temperatures [90]. Slip in diamond cubic structures occurs on the \{111\} planes.

In order to analyse slip in the systems considered in our investigations we use the concept of slip vector [91]. The slip vector for atom \(i\) is given by

\[
\mathbf{s}_i = -\frac{1}{N_s} \sum_{j \neq i}^{N_m} (\mathbf{r}_{ij} - \mathbf{r}_{ij}^0), \quad (4.2)
\]

\[
\bullet \text{ Nearest neighbours of atom } i \text{ in their reference positions}
\]

\[
\circ \text{ Nearest neighbours of atom } i \text{ in their current positions}
\]

\[
\bigcirc \text{ Atoms outside the list of nearest neighbours of atom } i
\]

Figure 4.10: Figure illustrating the atoms that contribute in the calculation of the slip vector for atom \(i\).
where $\mathbf{r}_{ij}$ and $\mathbf{r}_{ij}^0$ are the vectors linking atom $i$ and all its $N_{nn}$ nearest neighbours $j$ in their current and reference (prior to the indentation and scratching) positions, respectively. $N_s$ stands for the number of slipped neighbours. Fig. 4.10 illustrates the atoms that contribute in the calculation of the slip vector for atom $i$.

### 4.3.6 Cross slip

In general, screw dislocations tend to move in certain crystallographic planes. In face-centred cubic metals the screw dislocations move in $\{111\}$ type planes, but can switch from one $\{111\}$ type plane to another. This process is known as the cross slip, which is basically the transfer of glide of a screw dislocation from one slip plane to another during deformation or thermal recovery.
Chapter 5

Nanofriction Models

5.1 Introduction

In this thesis, we have employed three different simulation models to study distinctive aspects of friction at the atomic-scale. We call these models the steady-state model, the spring model, and the finite temperature model, which will be discussed in a more detailed manner in this chapter. Nanoindentation, nanoscratching and wear testing with an AFM cantilever are useful for characterising the mechanical properties of different sample materials. The intent behind the steady-state model was to use a simple procedure to study friction on the nanoscale in order to gain an understanding of particular microscopic phenomena, which would in turn also help to interpret some of the observations made during experiments with the AFM. Thus, the steady-state model bears a close similarity to the AFM and consists of a pyramidal indenter and a substrate. The indenter is initially moved in the vertical direction in order to indent the substrate. This is then followed by a movement in the horizontal direction to scratch the substrate surface. In the steady-state model the indenter is translated with a pre-specified velocity. Simulations using this model were started at 0 K and the atoms in the system were damped using
the Lindhard-Scharff inelastic energy loss model [92] in order to remove any surplus energy added to the system. This model was employed during the initial stage of this research and it has allowed us to investigate the effect of tip orientation and indentation depth on the friction coefficient, contact pressure, scratch hardness and the pile-up behaviour. The spring model is an improved version of the steady-state model, whereby the dynamics of springs in the horizontal (x) and vertical (y) directions were incorporated into the model in order to mimic the role of the cantilever in the AFM, used for the experiments. The spring model was developed to investigate the atomic-scale stick-slip phenomenon. The finite temperature model is basically very similar to the spring model, except that simulations using this model were started at 300 K and the temperature of the system is controlled and kept at 300 K using the Nosé-Hoover thermostat. An extension to the spring model was also implemented, in that the indenter was allowed to move in the lateral (z) direction.

5.2 Indenter Specification

The diamond indenter has the configuration of a 90° triangular-based pyramid comprising of three intersecting {001} faces. The pyramidal indenter is truncated from a cubic diamond lattice, as shown in Fig. 5.1. The three faces ABC, ACD and BCD constitute the total contact area of the tip, and meet at the vertex C. The tip is positioned such that the line CH is normal to the substrate surface. Therefore the tip manoeuvres with the {111} planes parallel to the face of the substrate sample. The length of the sides of the triangular plane ABD is denoted by $a$.

The indenters that are employed in the experiments are not atomically sharp and the apex will have a certain curvature. Therefore, to more closely
5.2 Indenter Specification

Figure 5.1: Schematic of the geometry of the indenter.

Figure 5.2: Plan view of the diamond indenter, comprising of \( \approx 4000 \) atoms, showing the dimer reconstruction of the three \{001\} faces together with the rounded apex.
model the experiments we have generated an indenter where the tip is rounded by the truncation of a number of atoms at the apex [93]-[99]; this can be observed in the plan view of the indenter shown in Fig. 5.2. The tip also has dimer reconstructed \{100\}(2 \times 1) surfaces which are more stable than the truncated crystal. The top three layers (i.e., the \{111\} planes) of the indenter are held fixed in the MD simulations.

5.3 Substrate Specification

The substrate takes the form of a rectangular lattice and we have employed fcc silver, bcc iron, silicon and hydrogen-terminated silicon as substrates in the friction studies in this thesis. The boundary conditions on the substrate atoms vary depending on the simulation model employed in the MD simulations. A detailed discussion of the boundary conditions employed in the different simulation models is given in Section 5.8. In all the models fixed boundary conditions are applied to the outer two layers of the substrate in the x and z directions (i.e., the edge atoms) to restrict the vertical or horizontal motion of the computational cell.

5.4 Steady-state Model

The diagram in Fig. 5.3 shows a schematic of the indentation/scratching model used in the initial MD simulations, performed during the early stage of this research. This model is referred to as the steady-state model. It illustrates the configuration of the tip and the substrate in the system under consideration. The simulation consists of three stages, namely: the indentation of the substrate, the relaxation of the system; followed by the scratching of the substrate. The tip is positioned such that the line AB (line from the apex of the
5.4 Steady-state Model

tip to the base) is normal to the substrate surface (Fig. 5.3) and it operates with the \{111\} planes parallel to the face of the substrate. At the beginning of the indentation, the vertex of the indenter is positioned above and at one end of the substrate surface (Fig. 5.3). It is placed at a height of 5 Å above the substrate surface which is outside the cut-off range of the tip-substrate interaction potential. When the apex of the indenter has reached the substrate surface, the substrate is then indented to the required indentation depth. All simulations performed using the steady-state model are started at 0 K and the Lindhard-Scharff inelastic energy loss model [92] is used to damp atoms in the system so that the temperature of the tip and the substrate does not rise excessively and stabilises at a low value.

![Figure 5.3: Schematic representation of the steady-state model used in the MD simulations showing the direction of indentation and the direction of scratching.](image)

5.4.1 Nanoindentation Simulation

For each timestep of the indentation simulation we impart a sinusoidal displacement, \(y(t)\), on the fixed top layer atoms of the indenter, which is given
Nanofriction Models

by

\[ y(t) = y_{\text{max}} \sin \left( \frac{\pi t}{T_I} \right), \quad (5.1) \]

where \( y_{\text{max}} \) is the maximum displacement of the constrained indenter atoms from its initial position above the substrate in a direction perpendicular to the substrate surface, \( T_I \) is the indentation period (i.e., equal to half of the sine period) and \( t \) is the time elapsed. Initially, the indenter atoms have an assigned velocity of \( y_{\text{max}} \pi / T_I \). Thus, the displacement of the constrained top layer atoms governs the motion of the indenter. At the end of the indentation simulation the whole system is relaxed by setting the velocity of the fixed atoms of the indenter to be zero in the time interval of \( T_I < t \leq T_{\text{rel}} \), before starting the scratching simulation. Here \( T_{\text{rel}} \) is the time at which the relaxation process ends.

5.4.2 Nanoscratching/Nanofriction Simulation

During the scratching simulation the indenter is displaced in the horizontal direction by giving a velocity to the fixed top-layer atoms of the indenter (i.e., top three layers in the \{111\} planes). The horizontal motion of the indenter is modelled in two different ways:

1. Model I: Horizontal displacement expressed as a cosine function,

2. Model II: Linear increase followed by constant velocity and linear decrease.

Model I: Horizontal displacement expressed as a cosine function

In this model, the indentation process is carried out in exactly the same way as described in Section 5.4.1. For each timestep of the scratching simulation we impart a displacement, \( x(t) \), on the fixed top layer atoms of the indenter,
5.4 Steady-state Model

which is given as

\[ x(t) = x_{\text{max}} \left[ 1 - \cos \left( \frac{\pi t}{T_S} \right) \right], \quad (5.2) \]

where \( x_{\text{max}} \) is the maximum displacement of the constrained indenter atoms in the horizontal direction from its initial \( x \)-position (i.e., at the end of the indentation and relaxation phase and the beginning of the scratching phase). Moreover, \( T_S \) is the scratching period and \( t \) is the time elapsed.

By differentiating Eq. 5.2, we obtain an expression for the velocity, which is given by

\[ v(t) = \frac{\pi}{T_S} x_{\text{max}} \sin \left( \frac{\pi t}{T_S} \right), \quad (5.3) \]

By substituting \( t = T_S/2 \) in Eq. 5.3 we obtain the maximum velocity of the indenter during the scratching period, which is given by \( v_{\text{max}} = (\pi/T_S) x_{\text{max}} \).

![Figure 5.4](image)

Figure 5.4: Graph showing the description of the velocity of the top fixed indenter atoms during the scratching simulation for (a) model I and (b) model II.

Model II: Linear increase followed by constant velocity and linear decrease

This model is just an alternative version of Model I, where the velocity of the fixed layers of the indenter during the scratching simulation is described as
Nanofriction Models

follows:

\[ v(t) = \begin{cases} \frac{5v_{\text{max}}}{T_s} t, & 0 \leq t \leq \frac{1}{5} T_s \\ v_{\text{max}}, & \frac{1}{5} T_s < t < \frac{4}{5} T_s \\ v_{\text{max}} - \frac{5v_{\text{max}}}{T_s} (t - \frac{4}{5} T_s), & \frac{4}{5} T_s \leq t \leq T_s \end{cases} \]  

(5.4)

where \( v_{\text{max}} \) is the maximum velocity and \( v_{\text{max}} = (5/4T_s) x_{\text{max}} \). During the scratching simulation, for the first one-fifth of the scratching period the velocity increases linearly from zero and then for the next three-fifth of the scratching period it remains constant. For the last fifth of the scratching period the velocity decreases linearly until it reaches zero.

Figs. 5.4(a) and 5.4(b) show a graphical representation of the description of the velocity during the scratching simulation when employing model I and model II, respectively. The description of the velocity in Model II allows us to calculate the coefficient of friction when the system has reached a steady-state regime and this is the reason why we have employed this model rather than model I.

5.5 Spring Model

Fig. 5.5 shows a diagrammatic representation of the spring model employed in the MD simulations to investigate the stick-slip phenomena on the atomic-scale. The model consists of an indenter attached to two springs, positioned in the horizontal (\( x \)) and vertical (\( y \)) directions. The horizontal and vertical springs are attached to support blocks A and B.

The idea is that for both the indentation and scratching, instead of giving the fixed indenter atoms a specified displacement at each timestep (as in the steady-state model), we try to displace the indenter by means of a spring
5.5 Spring Model

Figure 5.5: Schematic representation of the spring model. The indenter is attached to two springs in the vertical (indentation) and horizontal (scratching) directions. The horizontal and vertical springs are attached to support blocks A and B, respectively.

positioned appropriately. Therefore, compression of the vertical ($y$) spring will cause the displacement of the indenter during the indentation process, whereas stretching of the horizontal ($x$) spring will cause the indenter to displace during the scratching simulation. All simulations performed using the spring model are started at 0 K and atoms in the system are damped using the Lindhard-Scharff inelastic energy loss model [92] in order to remove any surplus energy added to the system during the indentation and the scratching processes.

The spring model was developed because it is a more realistic model of the experiment compared to the steady-state model. It is still not exactly what happens in the practical device, where the vertical force is held fixed by use of a transducer. In our spring model the vertical force can vary.

5.5.1 Indentation

In performing the simulations, the springs are assumed to be connected to the top \{111\} plane of tip atoms. These atoms are treated as a point mass
that move together and experience an integrated vertical force $F_y$ from all the other indenter atoms below and also a force from the attached spring. During the indentation phase the fixed atoms are constrained in the horizontal ($x$) direction. The equation of motion of this point mass is therefore

$$ma_y(t) = F_y(t) + k_y (y_B(t) - y(t)),$$

(5.5)

where $a_y(t)$ is the vertical acceleration of the indenter atoms at time $t$, $m$ is the mass of the tip and $y(t)$ is the vertical displacement of the indenter at time $t$. The term $k_y (y_B(t) - y(t))$ is the spring force on the indenter, where $k_y$ is the spring constant or the force constant of the vertical spring measuring the stiffness of the spring. The displacement of the vertical support B shown in Fig. 5.5 at each timestep of the indentation simulation is given by $y_B(t) = V_B t$ and $y_B(t) = y_{\text{max}} = V_B T_I$, for $T_I < t \leq T_{rel}$. After the indentation, $t > T_I$, the whole system is relaxed.

### 5.5.2 Scratching

The relaxation phase is then followed by the scratching part of the simulation. During the scratching, the fixed layer of indenter atoms are displaced in the horizontal ($x$) direction by motion of the support A but are constrained in the lateral ($z$) direction. The support A is set in motion with a constant speed $V_A$ in the $x$ direction for $t > T_{rel}$ and thus the equations of motion are given as

$$ma_x(t) = F_x(t) + k_x (V_A t - x(t)),$$

(5.6)

and

$$ma_y(t) = F_y(t) + k_y (y_{\text{max}} - y(t)),$$

(5.7)
5.5 Spring Model

where \( a_x(t) \) is the horizontal acceleration of the indenter atoms, \( x(t) \) is the horizontal displacement of the indenter at time \( t \). The displacement of the support A during the scratching simulation can be written as \( V_A t \). Moreover, \( k_x \) is the spring constant of the horizontal spring and \( F_x(t) \) is the frictional force in the horizontal direction.

5.5.3 Calculating the damping constant

Consider the equation of motion

\[
mx(t) = -bx(t) - k_xx(t),
\]

where \( b \) is the damping constant. We need to find an expression for \( b \) in terms of the other known parameters. Therefore, rearranging Eq. 5.8, we get

\[
mx(t) + bx(t) + k_xx(t) = 0, \quad (5.9)
\]

which is a second-order differential equation for a damped harmonic oscillator. To solve this equation, we substitute \( \gamma = b/2m \) and \( \omega_0^2 = k_x/m \) to obtain

\[
\dot{x}(t) + 2\gamma \dot{x}(t) + \omega_0^2 x = 0. \quad (5.10)
\]

We try an exponential solution of the form \( x = e^{\lambda t} \) and substituting in Eq. 5.9, we get

\[
e^{\lambda t} (\lambda^2 + 2\gamma \lambda + \omega_0^2) = 0. \quad (5.11)
\]

Since \( e^{\lambda t} \neq 0 \), we must have \( \lambda^2 + 2\gamma \lambda + \omega_0^2 = 0 \), and this auxiliary equation has the roots \( \lambda_1 = -\gamma + \sqrt{\gamma^2 - \omega_0^2} \) and \( \lambda_2 = -\gamma - \sqrt{\gamma^2 - \omega_0^2} \). Now, for the case of critically damped we need the condition \( \gamma^2 - \omega_0^2 = 0 \), where \( \lambda_1 \) and \( \lambda_2 \) are real and equal roots. From this condition, we obtain the expression for the
damping constant $b$, which is

$$b = 2 \sqrt{k_x m}.$$

To decrease the amplitude of the unwanted oscillations during the scratching simulations, we damp them. Therefore, during the scratching simulation the equations of motions in the $x$ and $y$ directions are given by

$$ma_x(t) = F_x(t) + k_x (V_A t - x(t)) + b (V_A - \dot{x}(t)),$$  \hspace{1cm} (5.12)

and

$$ma_y(t) = F_y(t) + k_y (y_{\text{max}} - y(t)),$$ \hspace{1cm} (5.13)

respectively.

Some tests were carried out to try to determine a reasonable value for a damping constant for the springs. However, the stick-slip phenomenon was found to be very sensitive to the value of the damping constant with too large a value resulting in a rigid spring with no stick events and smaller values giving results which were qualitatively similar to those with no damping. As a result no damping was included in our simulations.

### 5.6 Finite Temperature Model

Fig. 5.6 shows a schematic representation of the finite temperature model. The model consists of an indenter attached to three springs, positioned in the horizontal ($x$), vertical ($y$) and lateral ($z$) directions. The horizontal, vertical and lateral springs are attached to support blocks A, B and C, and have spring constants $k_x$, $k_y$, and $k_z$, respectively. This model mimics the role of the cantilever in the Atomic Force Microscope (AFM), used for the experiments. Unlike the steady-state model and the spring model, in this
5.6 Finite Temperature Model

Figure 5.6: Schematic representation of the finite temperature model. The indenter is attached to three springs in the horizontal (x), vertical (y), and lateral (z) directions. The horizontal, vertical and lateral springs are attached to support blocks A, B and C, respectively.

model the effect of temperature is more accurately considered. The simulations using the finite temperature model were all started at a temperature of 300 K and the Nose-Hoover thermostat (discussed in Section 5.7) was employed to control the temperature and keep the temperature of the system at 300 K. The corresponding boundary conditions of the system employed in these simulations at 300 K are discussed in more detail in Section 5.8.

The three springs are assumed to be connected to the atoms of the top (111) plane of the indenter atoms. During the indentation phase the fixed atoms are constrained in the horizontal (x) and lateral (z) directions. Thus, the equation of motion of the indenter during indentation is given by Eq. 5.5.

During the scratching stage, the fixed layer of indenter atoms are displaced in the horizontal (x) direction by motion of the support A. In addition the motion of the indenter is unconstrained in the z-direction, while support C is kept fixed in the z-direction. Thus the equations of motion during the
scratching phase are given by

\[
ma_x(t) = F_x(t) + k_x (V_A t - x(t)),
\]

(5.14)

\[
ma_y(t) = F_y(t) + k_y (y_{\text{max}} - y(t)),
\]

(5.15)

\[
ma_z(t) = F_z(t) - k_z (z(t)).
\]

(5.16)

In Eqs. 5.14–5.16, the forces \(F_x(t)\), \(F_y(t)\) and \(F_z(t)\) are the integrated forces arising from the action of the other indenter atoms with the fixed top-layer atoms of the tip in the horizontal \((x)\), vertical \((y)\) and lateral \((z)\) directions, respectively.

### 5.7 Temperature Control

In classical MD simulations, the temperature of the system is proportional to the total kinetic energy of the atoms. In a macroscopic system, the environment surrounding the region of tribological interest acts as an infinite heat sink, removing excess energy and helping to maintain a fairly constant temperature. However, systems undergoing sliding friction or indentation require work to be performed on the system, which raises its energy and causes temperature to increase. Ideally, a sufficiently large simulation would be able to model the same behaviour observed macroscopically. But while the thousands of atoms at an atomic-scale interface are within reach of computer simulation, the \(O(10^{23})\) in the experimental apparatus are not. Hence the surplus energy added to the system through the indentation and scratching processes is 'trapped' in the computational box. This, therefore, leads to the system heating up, which may in turn affect the physical properties of the material resulting in unrealistic behaviour of the material under investigation or even melting within the system if the temperature is too high. There are numerous
thermostats available to control the temperature of the system, but a simple and straightforward approach is to damp the motion of some selected atoms in the system.

5.7.1 Damping

The dynamics of the selected damped atoms in the system evolve according to Newtonian mechanics, but the velocities are periodically re-scaled according to some energy loss model. For our steady-state and spring models, we have employed the Lindhard-Scharff inelastic energy loss model [92] to damp selected atoms in the systems employing the steady-state and spring model to fix the kinetic temperature of these systems. At each timestep the positions and velocities of damped atom \( i \) are re-scaled as:

\[
\mathbf{r}_i = \mathbf{r}_i - r_n \mathbf{v}_i, \quad (5.17)
\]

\[
\mathbf{v}_i = v_n \mathbf{v}_i, \quad (5.18)
\]

where \( \mathbf{r}_i \) and \( \mathbf{v}_i \) are the position and velocity vectors of atom \( i \). In addition, \( r_n \) and \( v_n \) are the factors by which the positions and velocities are re-scaled and \( n \) is the number of species in the system. For our case, \( n = 1 \) for damped C atoms, whereas \( n = 2 \) for damped Ag atoms. In the simulations where we have employed the Lindhard-Scharff inelastic energy loss model, \( v_1 = 0.996654, r_1 = 1.672927 \times 10^{-3} \) (for damped C atoms) and \( v_2 = 0.998942, r_2 = 5.290476 \times 10^{-4} \) (for damped Ag atoms).

5.7.2 Thermalisation

When performing a MD simulation where we want to more accurately model the experiment, a choice must be made as to which thermodynamic ensemble to
study. These ensembles are distinguished by which thermodynamic variables are held constant over the course of the simulation. It is quite natural to keep the number of atoms \( N \) and the volume of the simulation cell \( V \) constant over the course of a MD simulation. In addition, for a system without energy transfer, integrating the equations of motion will generate a trajectory over which the energy of the system \( E \) will also be conserved. A simulation of this type is thus performed in the constant-\( NVE \), or microcanonical, ensemble.

In our case a thermodynamic ensemble that will more closely resemble reality will be one in which the temperature \( T \), rather than the energy, is held constant. These simulations are performed in the constant-\( NVT \), or canonical, ensemble. A constant temperature is maintained in the canonical ensemble by using any of a large number of thermostats.

A sophisticated approach to maintaining a given temperature is through Langevin dynamics. Originally used to describe Brownian motion, this method has found widespread use in MD simulations. In this approach, additional terms are added to the equations of motion, corresponding to a frictional term and a random force. The equations of motion are given by

\[
ma = F - m\xi v + R(t),
\]

where \( F \) are the forces due to interatomic potential, the quantities \( m \) and \( v \) are the particle mass and velocity, respectively, \( \xi \) is a friction coefficient, and \( R(t) \) represents a random "white noise" force. The random force can be given by a Gaussian distribution.

As with any thermostat, the atom velocities are altered in the process of controlling the temperature. It is important to keep this in mind when using a thermostat, because it has the potential to perturb any dynamic properties of the system being studied. To help avoid this problem, one effective approach is to add Langevin forces only to those atoms in a region away from where the
5.7 Temperature Control

dynamics of interest occurs. In this way, coupling to a heat bath is established away from the important action and simplified approximations for the friction term can be used without unduly influencing the dynamics produced by the interatomic forces. Coupling to a heat bath mimics the heat sink of the system.

In the MD simulations employing the finite temperature model, the temperature of the system is maintained at a fairly constant temperature through the use of the Nosé-Hoover thermostat.

**Nosé-Hoover Thermostat**

A thermostat that corresponds rigorously to a canonical ensemble has been developed by Nosé [100]. This significant advance also adds a friction term, but one that maintains the correct distribution of vibrational modes. It achieves this by adding a new dimensionless variable to the standard classical equations of motion that can be thought of as a large heat bath, which couples to each of the physical degrees of freedom. The actual effect of the variable, however, is to scale the coordinates of either time or mass in the system. The dynamics of the expanded system correspond to the microcanonical ensemble, but when projected onto only the physical degrees of freedom they generate a trajectory in the canonical ensemble. Sampling problems associated with the very small or very stiff systems can be overcome by attaching a series of these Nosé-Hoover thermostats to the system [101]. The resulting equations of motion are time reversible, and the trajectories can be analysed exactly with well-established statistical mechanical principles [101]. For a complete description of the Nosé thermostat and its relation to other formalisms for generating classical equations of motion, the reader is referred to Hoover [102].

The Nosé-Hoover equations of motion are given by

\[ \dot{r}_i = \frac{P_i}{m_i}, \]  

(5.20)
\[ p_i = -\frac{\partial U (r^N)}{\partial r_i} - \xi p_i, \]  
(5.21)

\[ \dot{\xi} = \left( \sum_i \frac{p_i^2}{m_i} - \frac{g}{\beta} \right) / Q. \]  
(5.22)

In terms of variables used in Eqs. 5.20–5.22, \( \mathcal{H} \) reads as

\[ \mathcal{H}_{\text{Nosé}} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U (r^N) + \frac{\xi^2 Q}{2} + \frac{g s}{\beta}, \]  
(5.23)

where \( p_i \) and \( r_i \) are the momenta and coordinates of particle \( i \) in the system of \( N \) particles, respectively. In addition, \( m_i \) is the mass associated with particle \( i \), \( \xi \) is the thermodynamic friction coefficient, \( s \) is an additional coordinate introduced by Nosé in the Hamiltonian and \( Q \) is an effective "mass" associated to \( s \), the parameter \( g \) is fixed as \( g = 3N \). In Eq. 5.22, \( \beta = 1 / (k_B T) \), where \( k_B \) is the Boltzmann’s constant and \( T \) is the temperature.

The equations of motion (Eqs. 5.20–5.22) are unique, in the sense that other equations of the same form cannot lead to a canonical distribution. The equations of motion (Eqs. 5.20–5.22) are integrated using the velocity Verlet algorithm. The first step of the velocity Verlet algorithm is:

\[ r_i (t + \Delta t) = r_i (t) + v_i (t) \Delta t + \left[ \frac{f_i (t)}{m_i} - \xi (t) v_i (t) \right] \frac{\Delta t^2}{2}, \]  
(5.24)

\[ v_i (t') = v_i (t) + \left[ \frac{f_i (t)}{m_i} - \xi (t) v_i (t) \right] \frac{\Delta t}{2}, \]  
(5.25)

\[ \xi (t') = \xi (t) + \left[ \sum_i m_i v_i^2 (t) - gT \right] \frac{\Delta t}{2Q}, \]  
(5.26)
5.8 Boundary Conditions

The second step of the velocity Verlet algorithm is:

\[
v_i(t + \Delta t) = v_i(t') + \left[ \frac{f_i(t + \Delta t)}{m_i} - \xi(t + \Delta t) v_i(t + \Delta t) \right] \frac{\Delta t}{2}, \tag{5.27}
\]

\[
\xi(t + \Delta t) = \xi(t') + \left[ \sum_i m_i v_i^2(t + \Delta t) - gT \right] \frac{\Delta t}{2Q}. \tag{5.28}
\]

Additionally,

\[
\xi(0) = 0.
\]

Note that \(f_i(t)/m_i = a_i(t)\) is the acceleration of particle \(i\) in Eqs. 5.24–5.28 and that \(v(t + \Delta t/2) \equiv v(t')\). The value of \(Q\) employed in our simulation is \(Q = gT\tau\), where \(\tau\) is a typical relaxation constant and \(0.5 < \tau < 2.0\) ps. We have taken \(\tau = 1\) ps.

5.8 Boundary Conditions

The computational box is usually generated by an algorithm which executes repetitions of the unit crystal cell along each dimension until the required system size is obtained. The constraints of computer power force MD simulations to employ small systems of atoms. No matter how large the simulated system is, its number of atoms, \(N\), would be negligible compared with the number of atoms contained in a macroscopic piece of matter (of the order of \(10^{23}\)). Hence it is important to choose a computational cell large enough to minimise any finite-size effects. Boundary conditions are thus employed to maintain as accurately as possible the realistic physical behaviour of the simulated material. Thus, boundary conditions aid in imitating the influence of the bulk material surrounding the computational cell.

Different types of boundary conditions are applied to the surfaces of the computational box, depending on the type of investigations being carried out.
Figure 5.7: Schematic diagram of the typical boundary conditions (imposed on both the substrate and indenter) utilised in the nanoindentation and nanoscratching simulations. The boundary conditions in (a) are utilised in the steady-state and the spring model, where the simulations were started at 0 K and conditions in (b) are employed in the finite temperature model where the whole system was heated to a certain specified temperature and the system is kept at that temperature using the Nosé-Hoover thermostat.
5.8 Boundary Conditions

Either free boundaries, fixed or rigid boundaries or periodic boundaries are routinely used. Free boundary conditions are applied to an atom when there are no restrictions on the dynamics of that atom, whereas fixed boundary conditions are usually applied to edge atoms to constrain the motion of the computational cell in any of the Cartesian directions. In periodic boundary conditions (PBC), the system of atoms is typically box-shaped, and is conceptually repeated to fill space. Thus any atoms drifting out of the simulation space re-enter the space on the opposite side with the same velocity and direction. Periodic boundary conditions are thus applied to the sides of the computational box to minimise any edge effects that can stem from atoms at the edges of the computational cell, which behave differently than those in the bulk and to prevent atoms from escaping from the simulations.

Simulations performed employing the steady-state model and the spring model, were all started at 0 K. The boundary conditions imposed on the system in these simulations are illustrated in Fig. 5.7(a). Fixed boundary conditions are applied to the outer two layers of the substrate in the x and z directions. The remaining substrate atoms are damped (using the Lindhard-Scharff inelastic energy loss model [92]) to remove any surplus of energy added to the system by the indenter during the indentation and the scratching processes. As for the indenter, the top \{111\} planes of tip atoms are kept fixed. These fixed indenter atoms move together during the indentation and the scratching simulations and they experience integrated vertical and horizontal forces from all the damped atoms in the indenter below.

The corresponding boundary conditions of the system employed in the simulations using the finite temperature model are shown in Fig. 5.7(b). Here, fixed boundary conditions are applied to the outer two layers of the substrate in the x and z directions, to the bottom layer of the substrate and to the top layers of the indenter in the \{111\} plane. Here, the fixed atoms are those
atoms that are at 0 K and the remaining atoms are all thermalised at 300 K. The thermostat atoms are the atoms that are attached to the Nosé-Hoover thermostat (discussed in Section 5.7) to control the temperature and keep the temperature of the system at 300 K. The systems employing the finite temperature model consist of 5 layers of the thermostat atoms in the $x$ and $z$ directions and 3 layers in the $y$ direction.
Chapter 6

Results from the Steady-State Model

6.1 Introduction

In this chapter, the nanoscale ploughing friction and wear behaviour of a pyramidal diamond indenter sliding against a face-centred cubic silver (100) surface is investigated by means of parallel MD simulations of nanoindentation followed by nanoscratching. The simulations are started at 0 K and any surplus energy added to the system due to the dynamics during the nanoindentation and nanoscratching processes is removed using an energy loss model. The relationship between the friction coefficient, the contact pressure, the scratch hardness and the indenter orientation is studied. The simulations are performed using three different indenter orientations. The behaviour of the coefficient of friction and the hardness is also investigated as a function of indentation depth, where simulations are performed for one of the tip orientations at three different depths.

On the experimental front, we compare our results with investigations that have been performed on polycrystalline bulk silver samples and silver single
Results from the Steady-State Model

crystal using two different devices, namely, the Triboscope and the NanoScan. The effect of tip orientations at varying normal loads is also studied. The aim of these investigations is to provide a good comparison to the results obtained from the MD simulations.

6.2 Details of the Simulation

Different indenter and substrate sizes are employed in the MD simulations, depending on the penetration depths. This is done to avoid wear debris (particles which become detached from the worn away surface) protruding over the indenter and also to increase the efficiency in use of the computing resources. The simulations in this chapter were performed using three different orientations of the indenter as shown in Fig. 6.1. For each orientation, simulations were carried out at an indentation depth of 5 and 10 Å. One further simulation was performed at a penetration depth of 30 Å, using orientation (III) of the tip.

![Diagram of three orientations](image)

Figure 6.1: The top view of the three orientations of the indenter used in the simulations. The crystallographic directions given are of the underlying substrate lattice.
6.2 Details of the Simulation

6.2.1 System Specifications

Table 6.1 gives the relevant information, including the number of indenter and substrate atoms and the dimensions of the substrate that are employed in the different MD simulations. A smaller indenter of ~8400 atoms was utilised for the shallow indent of 5 Å and bigger tips of ~30,400 and ~64,400 atoms were employed for the indentation depths of 10 and 30 Å, respectively. The smaller indenter had a smaller radius of curvature than the two other indenters, which had approximately the same radius of curvature, all three indenters were of different heights. The results are still comparative because the friction coefficient is independent of the height of the indenter. Due to the restriction in the available computational power, the systems used in our simulations are smaller compared to those employed in the experiments. As a result, the simulations comprise of penetration depths and scratching lengths which are of an order of magnitude smaller than the experimental values and the simulation times are several orders of magnitude smaller.

Table 6.1: Table showing the size of the indenter and the substrate for the different MD simulations performed using the steady-state model.

<table>
<thead>
<tr>
<th>Indentation Depth (Å)</th>
<th>Number of Indenter atoms</th>
<th>Dimensions of substrate (Å³)</th>
<th>Number of substrate atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8432</td>
<td>420 ×60 ×150</td>
<td>228,660</td>
</tr>
<tr>
<td>10</td>
<td>30,369</td>
<td>420 ×100 ×210</td>
<td>504,288</td>
</tr>
<tr>
<td>30</td>
<td>64,373</td>
<td>420 ×100 ×210</td>
<td>504,288</td>
</tr>
</tbody>
</table>

6.2.2 Speed of Nanoindentation and Nanoscratching

The indentation simulations at the indentation depths of 5, 10 and 30 Å were run for an indentation period of 25 ps, 37.5 ps and 87.5 ps, respectively. Hence, the tip moved at an average maximum velocity of 40 ms⁻¹ during the inden-
Results from the Steady-State Model

tation simulations. After the indentation simulation, the whole system was relaxed for a period of 5 ps. The indenter was then displaced horizontally by a distance of approximately 210 Å in 150 ps, which implies that the maximum velocity of the tip during the scratching simulations was 140 ms⁻¹.

6.3 Results

6.3.1 Effect of tip Orientation during Indentation

Fig. 6.2 shows the displacement-time plot obtained in the MD simulation of the indentation at a depth of 5 Å for the three different indenter orientations. The first 25 ps of the indentation phase of the simulation shows the stage where the indenter is being moved downwards, with the final 5 ps being the relaxation period. Changing the orientation of the indenter did not have a significant effect on the force on the tip during the indentation period, this can be observed in Fig. 6.3. The tip of the indenter was displaced approximately 8.7 Å from its initial y-position above the silver surface, thus 3.7 Å into the crystal. Since
6.3 Results

the displacement of the fixed top layer indenter atoms was specified to be 10 Å, this indicates that the apex compressed during the indentation simulation.

Fig. 6.3 shows that the force remains static in the load-displacement curve in the indentation region of 0.1–0.2 nm. This corresponds to the point where there is the first pile-up generation, i.e. a number of substrate atoms are pushed above the surface of the silver substrate. This causes a flattening of the curve as it allows stress relief. As a result there is significant volume and density changes induced in the region of the substrate underneath the indenter tip in a short time period. The substrate atoms underneath the indenter tip then relax to more favourable minimum energy configurations by re-arranging themselves. This rearrangement of atoms explains the observation of “pop-ins” in the force-depth curve, see Fig. 6.3. These pop-ins are also observed experimentally for other metals [103]-[105].

![Figure 6.3: Force-depth curve from the indentation simulation at an indentation depth of 5 Å, using the three different tip orientations.](image)

Figure 6.3: Force-depth curve from the indentation simulation at an indentation depth of 5 Å, using the three different tip orientations.
6.3.2 Effect of tip Orientation during Scratching

The results from the scratching simulations are presented, by analysing first the relation between the coefficient of friction and the orientation of the indenter; second, by studying the dependence of the friction coefficient and scratch hardness on the indentation depth. The normal and frictional forces are taken as the average of the forces, during the steady-state regime, in the vertical and horizontal direction, respectively. The scratching process starts at the end of the indentation and relaxation phase.

During the scratching simulation the effect of the tip orientation was found to be crucial. Figs. 6.4(a)–6.4(c) illustrate the damage to the surface of the substrate for the three different tip orientations at an indentation depth of 10 Å. During the tangential motion of the tip there is a ploughing effect. As a result of this ploughing, a certain volume of the surface material was removed and an abrasive groove was formed on the substrate surface. By comparing the three figures (Figs. 6.4(a)–6.4(c)), different degrees of abrasive wear of the substrate can be observed. The average normal and frictional forces for the three tip orientations and at indentation depths of 5 and 10 Å are summarised in Table 6.2. For indentation depths of 5 and 10 Å, i.e. the cases where the simulations were performed for all three tip orientations, the normal force is similar for all the three orientations. Therefore, by keeping the top layer of the indenter atoms fixed at a certain height above the surface we have achieved a normal force that is independent of the tip orientation. The frictional force, however, is highly dependent on the tip orientation.

The orientation of the tip has a considerable effect on the surface damage and consequently, on the coefficient of friction. During the scratching, the indenter ploughs through the substrate resulting in the piling-up of the substrate atoms in front of the indenter and at the side of its track. The indenter orientation determines the degree of pile-up in front of the indenter in each
Figure 6.4: Surface damage viewed from top without the indenter, at the end of the scratching phase, and at a penetration depth of 10 Å when (a) orientation (I) (b) orientation (II) and (c) orientation (III), is employed. The light coloured spheres around the edge of the hole represent piled-up substrate atoms on the surface.
Results from the Steady-State Model

Table 6.2: Results of MD simulations for the three orientations of the tip and at the indentation depths of 5 and 10 Å.

<table>
<thead>
<tr>
<th>Tip Orientation</th>
<th>Normal force (nN)</th>
<th>Frictional force (nN)</th>
<th>Friction coefficient</th>
<th>Height of pile-up (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indentation Depth of 5 Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>50.030</td>
<td>20.283</td>
<td>0.405</td>
<td>6.73</td>
</tr>
<tr>
<td>II</td>
<td>53.563</td>
<td>30.673</td>
<td>0.573</td>
<td>13.81</td>
</tr>
<tr>
<td>III</td>
<td>51.101</td>
<td>18.682</td>
<td>0.366</td>
<td>5.94</td>
</tr>
<tr>
<td>Indentation Depth of 10 Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>246.026</td>
<td>117.753</td>
<td>0.479</td>
<td>20.31</td>
</tr>
<tr>
<td>II</td>
<td>250.793</td>
<td>158.016</td>
<td>0.630</td>
<td>37.73</td>
</tr>
<tr>
<td>III</td>
<td>252.112</td>
<td>103.741</td>
<td>0.412</td>
<td>13.40</td>
</tr>
</tbody>
</table>

case. The height of the pile-up in front of the indenter is given in Table 6.2 for the different tip orientations at the indentation depths of 5 and 10 Å. As this pile up increases there is more resistance to motion. Therefore, a greater force is required to overcome this resistance which leads to an increase in the frictional force. The orientation of the tip thus determines the extent of abrasive wear of the silver substrate. This has a significant influence on the coefficient of friction, which varies from \( \sim 0.37 \) to \( \sim 0.57 \) and from \( \sim 0.41 \) to \( \sim 0.63 \) for an indentation depth of 5 Å and 10 Å respectively. The surface damage in Fig. 6.4(c), where orientation (III) was employed shows that there was less pile-up of the substrate atoms in front of the indenter. This in turn implies that there is less resistance to motion and a lower friction coefficient for this case. On the other hand, the friction coefficient was much higher when orientation (II) was employed (Fig. 6.4(b)), because there is more resistance to motion, this is due to the leading edge being the flat side of the tip. The friction coefficients in our simulations and those calculated in [46] were observed to be quite high compared with those observed experimentally [25], where extremely low friction coefficients of 0.005-0.015 were reported. A plausible explanation
for this might be that the substrates in MD simulations are completely free from defects. In the experiments, it is implausible that this was the case since there were extrinsic factors, such as surface contaminants, and issues such as the presence of dislocations, vacancies and surface roughness that need to be taken into consideration.

6.3.3 Analysis of Dislocations

No sub-surface defects were observed for the shallow indent of 5 Å. However, dislocations were observed for all three tip orientations at an indentation depth of 10 Å. Figs. 6.5(a)–6.5(f) are the top view of the silver substrate showing the dislocations during the initial stage of the scratching simulation, for the three orientations of the indenter at an indentation depth of 10 Å. Figs. 6.5(b), 6.5(d) and 6.5(f) are the same pictures as in Figs. 6.5(a), 6.5(c) and 6.5(e), respectively, except that atoms in Figs. 6.5(b), 6.5(d) and 6.5(f) are shaded with regards to depth and energy filtered, whereas the atoms in Figs. 6.5(a), 6.5(c) and 6.5(e) are shaded according to the slip vector modulus given by Eq. 4.2. For the pictures of the dislocations where the atoms are coloured according to the modulus of the slip vector, the colour scheme is the same as the one chosen by Rodríguez de la Fuente et al. [91] and is shown in the key in Fig. 6.5.

The red atoms show the region of the lattice that have undergone a perfect dislocation, i.e., dislocation with Burgers vector \( \mathbf{b} = \frac{1}{2} \langle 110 \rangle \). The green atoms represent the atoms on a stacking fault. The boundary in the plane of the fault, separating the faulted region from the perfect region of the lattice, is a partial dislocation. The partial dislocations are the Shockley partials, i.e., dislocations with Burgers vector \( \mathbf{b} = \frac{1}{6} \langle 112 \rangle \). Shockley partial is associated with slip, which occurred in the \{111\} planes and the observed slip direction is \langle 110 \rangle. For the case where orientation (II) is employed (Figs. 6.5(c) and 6.5(d)), more dislocations are observed compared to the cases where orientation (I)
Figure 6.5: Top view of the silver substrate at $t = 21$ ps of the scratching simulation and at an indentation depth of 10 Å for the three orientations of the indenter. Figures (a), (c) and (e) are shaded according to the slip vector modulus given in the key, whereas figures (b), (d) and (f) are shaded with regards to depth and the atoms are energy filtered.
6.3 Results

Figure 6.6: Side view of the silver substrate at the end of the scratching simulation for the three orientations of the indenter and at an indentation depth of 10 Å. The red atoms show the plane of atoms that have slipped a full \langle 110 \rangle vector and the green atoms indicate the stacking fault plane.
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(Figs. 6.5(a) and 6.5(b)) and orientation (III) Figs. 6.5(e) and 6.5(f) were employed. Figs. 6.6(a)–6.6(c) show the dislocations underneath the scratch groove at the end of the scratching process for the three tip orientations at an indentation depth of 10 Å. More sub-surface defects were observed in the case where orientation (II) was employed and very few dislocations were seen when orientation (III) was employed.

6.3.4 Pile-up Generation

Fig. 6.7 shows the number of substrate atoms forced to the substrate surface as pile-up, in front of the tip and at the side of its track, during the scratching simulation for the three orientations of the indenter and at an indentation depth of 10 Å. Although the coefficient of friction is smaller when orientation (III) is employed compared to orientations (I) and (II), the number of piled-up atoms is higher for that case. This is because during the scratching a lot of atoms piled up along both sides of the track of the indenter and there was
6.3 Results

hardly any pile-up in front of the indenter. As for orientation (I) the pile-up is distributed mostly on one side of the indenter’s track and in front of the indenter. For orientation (II) most of the pile-up is in front of the indenter and very few atoms are piled up on both sides of the indenter’s track.

6.3.5 Contact Pressure and Scratch Hardness

Two other important parameters that have been calculated are the contact pressure of the indenter on the substrate during indentation and the scratch hardness of the substrate. The contact pressure is defined as the ratio of the vertical force and the tangential contact area during the indentation and is given by

\[
\text{Contact pressure} = \frac{F_y}{(3\sqrt{3}/2) h^2},
\]

where \( F_y \) is the force arising from the interaction of the tip with the substrate in the vertical \( (y) \) direction. The tangential contact area is taken as the cross-sectional area of the indenter, which is \((3\sqrt{3}/2) h^2\) where \( h = d + l \), where \( d \) is the actual indentation depth and \( l \) is the length that has been truncated from the apex of the indenter to give the tip a certain radius of curvature.

Table 6.3: Information on the different indenters employed in the simulations.

<table>
<thead>
<tr>
<th>Indenter</th>
<th>Number of indenter atoms</th>
<th>Length truncated at apex, ( l ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8432</td>
<td>1.805</td>
</tr>
<tr>
<td>2</td>
<td>30,369</td>
<td>8.083</td>
</tr>
<tr>
<td>3</td>
<td>64,373</td>
<td>9.817</td>
</tr>
</tbody>
</table>

values of \( l \) for the three indenters employed in the simulations are tabulated in Table 6.3. The scratch hardness of the substrate is defined as the quotient of the average normal force \( F_y \) by the square of the average scratch width \( w \) [106]. The scratch width was measured directly from the picture at the end
of the scratching simulation. However, the factor $k$ of the equation usually employed, \textit{i.e.},

\[ \text{Scratch hardness} = k \frac{F_y}{w^2}, \quad (6.2) \]

for the calculation of the scratch hardness relative to a reference material is not considered in our investigation.

**Contact area during the indentation process**

In this section, the contact area of the indenter with the substrate, during the indentation process, is calculated. The area of contact during the indentation process is taken as the area of cross-section of the indenter (refer to Fig. 6.8).

![Figure 6.8: Schematic of the crystal geometry of the indenter.](image)

To obtain an expression for that area of contact we just need to calculate the area of $\triangle ABD$. Since $\triangle ABD$ is an equilateral triangle, thus area of $\triangle ABD = \left(\frac{\sqrt{3}}{4}\right) a^2$. The parameter $h$ corresponds to calculated indentation depth at the end of the indentation process for an atomically sharp tip and is given by $h = d + l$, where $d$ is the actual indentation depth and $l$ is the length that has been truncated from the apex of the indenter to give the tip a certain
6.3 Results

Figure 6.9: Schematic illustrating the different parameters employed in the calculation of the hardness values. The parameter $d$ is the actual indentation depth and $l$ is the length that has been truncated from the apex of the indenter to give the tip a certain radius of curvature. The calculated indentation depth for a perfect atomically sharp tip is given by $h$ and $h = d + l$.

radius of curvature. Fig. 6.9 illustrates the difference between the parameters employed for the calculation of the hardness values. To calculate the area of contact in terms of $h$ we need to find $a$ in terms of $h$. Consider the $\triangle ACF$, then $AC = a/\sqrt{2}$ and area of $\triangle AEG = a^2 / (4\sqrt{2})$. Since area of $\triangle AEG = area$ of $\triangle ACG$, therefore area of $\triangle ACG = a^2 / (4\sqrt{2})$. From this we can derive the relationship $a = \sqrt{6}h$. This now enables us to calculate the area of contact in terms of $h$, and by substituting $a$ by $\sqrt{6}h$ in the expression for the area of $\triangle ABD$, we obtain area of $\triangle ABD = (3\sqrt{3}/2) h^2$. Hence, the contact area during the indentation process is $\left(\frac{3\sqrt{3}}{2}\right) h^2$.

Figs. 6.10(a) and 6.10(b) show the variation of the contact pressure during the indentation for the three orientations of the indenter at the indentation depth of 5 and 10 Å, respectively. It can be observed that the contact pressure during the indentation process is dependent on the indenter orientation only for the shallow indent of 5 Å. But tip orientation does not have a significant effect on the contact pressure for the deeper indent of 10 Å. It can clearly be observed that Figs. 6.10(a) and 6.10(b) are not consistent and this is because the indenter utilised for the shallow indent of 5 Å has a smaller radius of
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curvature than the bigger tip employed for the simulations at 10 Å. Hence, the fact that the contact area during indentation is a function of the radius of curvature explains the inconsistency in Figs. 6.10(a) and 6.10(b).

![Graph showing the variation of the contact pressure for different orientations of the indenter.](image)

Figure 6.10: Variation of the contact pressure for the three orientations of the indenter and at an indentation depth of (a) 5 Å and (b) 10 Å, during the indentation simulation.

The values of the contact pressure at the end of the indentation phase (excluding the relaxation phase) and the scratch hardness for the three orientations of the indenter and at the three different indentation depths of 5 and 10 Å are given in Table 6.4. The value of the scratch hardness varies for the different orientations of the indenter. The scratch hardness is higher when
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Table 6.4: The contact pressure and scratch hardness of the silver substrate obtained from the MD simulations when the three orientations of the tip were employed and at the indentation depths of 5 and 10 Å.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Scratch width, ( w ) (Å)</th>
<th>Scratch hardness (G' Pa)</th>
<th>Contact pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Indentation Depth of 5 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>9.194</td>
<td>59.186</td>
<td>64.068</td>
</tr>
<tr>
<td>II</td>
<td>11.237</td>
<td>42.419</td>
<td>78.838</td>
</tr>
<tr>
<td>III</td>
<td>12.258</td>
<td>34.009</td>
<td>64.467</td>
</tr>
<tr>
<td></td>
<td>Indentation Depth of 10 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>23.495</td>
<td>44.569</td>
<td>29.686</td>
</tr>
<tr>
<td>II</td>
<td>26.559</td>
<td>35.554</td>
<td>30.193</td>
</tr>
<tr>
<td>III</td>
<td>30.645</td>
<td>26.846</td>
<td>27.408</td>
</tr>
</tbody>
</table>

orientation (I) is employed compared to the other two orientations, whereas the scratch hardness is lower when orientation (III) is employed. This can be explained by the fact that the scratch width when employing orientation (I) is smaller compared to the scratch width when employing orientations (II) and (III), this is due to a geometrical effect, which is illustrated in Fig. 6.11. The length AG is the scratch width when employing orientation (I).

Figure 6.11: The top view of orientation (I) of the indenter. Length AG denotes the scratch width when performing the simulation with orientation (I).
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Fig. 6.11 an angle of $-90^\circ$ and $90^\circ$ gives orientations (II) and (III), respectively. The scratch width when employing orientations (II) and (III) is given by the length BD, which is equal to $a$. Thus, $w = \sqrt{3}a/2$ for orientation (I), which is less than $w = a$ for the case of orientations (II) and (III).

6.3.6 Effect of Indentation Depth during Scratching

We shall now discuss the results obtained from the scratching simulations using orientation (111) and at the three indentation depths of 5, 10 and 30 Å. Fig. 6.12 shows the variation of the frictional force with time during the scratching simulation for the three different indentation depths. The frictional force is higher for the indentation depth of 30 Å compared to the shallow indents of 5 Å and 10 Å. As we go deeper a greater force is required for the indenter to continue moving. This in turn implies a greater frictional force. Table 6.5 shows that both the frictional force and the normal force increases as the penetration depth increases. It can also be seen from Table 6.5 that the friction coefficient is dependent on the penetration depth and it varies from
6.3 Results

\( \sim 0.37 \) to \( \sim 0.61 \). As we go deeper the coefficient of friction increases and this could be explained by the observation of the dislocation loops in the \{111\} planes for the deeper indents, i.e., the one at a penetration depth of 10 Å and 30 Å. Another contributory factor is the height of the pile-up in front of the indenter. The height of the pile-up for the depth of 5 Å is \( \sim 5.94 \) Å, whereas for the depth of 10 and 30 Å the height of the pile-up are \( \sim 13.40 \) Å and \( \sim 38.59 \) Å, respectively. Higher pile-up in front of the indenter implies greater resistance to motion.

Table 6.5: Results of MD simulations when employing orientation (III) of the indenter at the three different indentation depths.

<table>
<thead>
<tr>
<th>Indentation depth (Å)</th>
<th>Normal force (nN)</th>
<th>Frictional force (nN)</th>
<th>Friction coefficient</th>
<th>Height of pile-up (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>51.101</td>
<td>18.682</td>
<td>0.366</td>
<td>5.94</td>
</tr>
<tr>
<td>10</td>
<td>252.112</td>
<td>103.741</td>
<td>0.412</td>
<td>13.40</td>
</tr>
<tr>
<td>30</td>
<td>817.030</td>
<td>498.406</td>
<td>0.610</td>
<td>38.59</td>
</tr>
</tbody>
</table>

Table 6.6: The contact pressure and scratch hardness of the silver substrate obtained from the MD simulations at the three different indentation depths and when employing orientation (III) of the indenter.

<table>
<thead>
<tr>
<th>Indentation depth (Å)</th>
<th>Scratch width, ( w ) (Å)</th>
<th>Scratch hardness (GPa)</th>
<th>Contact pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>12.258</td>
<td>34.009</td>
<td>64.467</td>
</tr>
<tr>
<td>10</td>
<td>30.645</td>
<td>26.846</td>
<td>27.408</td>
</tr>
<tr>
<td>30</td>
<td>67.204</td>
<td>18.090</td>
<td>18.803</td>
</tr>
</tbody>
</table>

Table 6.6 shows the behaviour of the contact pressure during the indentation simulation, at the indentation depth of 5, 10, and 30 Å and when orientation (III) of the indenter was employed. It can be observed that the contact pressure varies considerably as a function of depth. This is because at the shallow depth of 5 Å the indenter is in the region of the substrate where
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it deforms elastically. Hence the contact pressure in this region is higher since the contact area is smaller due to elastic recovery of the substrate. But as we indent deeper (i.e. 15 Å) into the substrate the contact pressure decreases because in this region the substrate deforms plastically and therefore there is less elastic contribution in the calculation of the contact pressure. It is important to note that the average of the contact pressure is different at each indentation depth. Therefore, the average of the contact pressure cannot be taken as the hardness of the substrate because this will mean that the hardness of the same material varies with increasing indentation depth, which is physically incorrect. Thus, in order to find a constant value for the hardness of the substrate more simulations need to be performed at increasing indentation depths until a steady value occurs. In our simulations it has not yet reached this value even at 30 Å, the maximum depth used here. The calculated contact pressure is an order of magnitude higher than the experimental value; this is mainly due to the shallower indentation depths that are reachable. Komanduri et al. [46, 55] have attributed this to the size effect and to the possibility of plastic deformation being governed by the theoretical yield strength at such small indentation scales.

Table 6.6 shows the variation of the scratch hardness for the three different indentation depths. As we go deeper the scratch hardness decreases quite considerably. This has been observed earlier by Komanduri et al. [46]. This can be explained by the fact that the scratch hardness is given by \( F_y/w^2 \), where \( F_y \) is the average normal force during the scratching simulation and \( w \) is the scratch width, and \( F_y \propto h^s \), where \( 1 < s < 2 \), whereas \( w^2 \propto h^2 \) (\( h \) is the calculated indentation depth). The value of \( s \) is deduced as the gradient of the line of best fit by plotting \( \log F_y \) against \( \log h \). We found that \( s = 1.7 \). It is only an estimate since we had only three data points. More simulations need to be performed to determine an accurate value for \( s \). According to Hertzian
theory of contact mechanics $s = \frac{3}{2}$ (see Chapter 2, Section 2.2.1), which is close to our numerical value of $s$ and therefore supports our relation. Another possible interpretation would be the observation of the dislocation loops in the \{111\} planes for the deeper indents, \textit{i.e.}, the one at a penetration depth of 10 and 30 Å, whereas there are no dislocations for the shallow indent of 5 Å.

Figure 6.13: Top view of the substrate showing the dislocation loops in the \{111\} planes moving in the $<110>$ directions at $t = 25$ ps of the indentation simulation and when using orientation (III) of the indenter at an indentation depth of 30 Å. (a) The intersection of the stacking faults on two \{111\} planes and the atoms are coloured according to the slip vector. (b) The same dislocations but the atoms are filtered on energy and coloured on height.

Figs. 6.13(a)–6.13(b) and Figs. 6.14(a)–6.14(b) show the dislocations observed in the middle of the indentation process when orientation (III) was employed at an indentation depth of 30 Å. The stacking faults are very clear from these figures and each stacking fault is bounded by two Shockley partial dislocations. Fig. 6.15 show the dislocations observed at the end of the scratching process. In this figure, the dislocations are planes of atoms in the \{111\} planes that have slipped.
Figure 6.1.1: Figures showing the dislocation loops at $t = 25 \text{ ps}$ of the indentation simulation and when using orientation (111) of the indenter at an indentation depth of 30 Å. (a) View of the substrate from the bottom showing the Shockley partial dislocations and another dislocation in the form of a cube propagating in the $<110>$ directions. (b) Side view of the silver substrate showing the dislocation in the form of a cube moving in the $<110>$ directions. The atoms in both pictures have been coloured according to the slip vector.

Figure 6.1.5: Side view of the silver substrate at $t = 135 \text{ ps}$ of the scratching simulation, at an indentation depth of 30 Å and using orientation (111) of the indenter. The $z$-direction is the [100] direction.
6.4 Comparison with Experimental Results

Nanoindentation and nanoscratching experiments have been performed by our collaborators, Prof. Asta Richter [93]-[95], Michael Gruner and Alexander Soshnikov, on silver samples using two different devices:

(i) the NanoScan, designed for directly scratching, particularly, hard materials;

(ii) the Triboscope, which has the shape of a diamond cube corner and is a device specifically designed for nanoindentation experiments, and so scratching is only possible by non-standard use of this device.

6.4.1 Experiments using the Triboscope

The Triboscope has been employed for making scratches on polycrystalline bulk silver samples. Understandably, measurement of the scratches with the same tip employed for making the scratches might lead to blurred pictures and hence might cause some inaccuracies in the results. Therefore, the scratches have been scanned by an atomic force microscope with a silicon nitride tip.

The nanoindentations and nanoscratches have been performed using two different normal forces or loads: 150 and 225 $\mu$N. This normal force was kept constant during the experiments. The experiments have been carried out using four different orientations of the indenter at the two different loads. The four tip orientations are shown in Fig. 6.16. Orientations (I)', (II)' and (III)' are similar but not exactly the same as the tip orientations (I), (II) and (III) of the MD simulations due to the difficulty of orientating the tip exactly in the way as used in the simulation model. Moreover, orientation (IV)' is similar to the orientation (I)' and orientation (I) employed in the experimental investigations and in the MD simulations, respectively. In addition, in the experiments there is a 2 or 3 degree mismatch with the 'perfect' orientation used in the MD
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Figs. 6.17(a) and 6.17(b) show the scratches in the four different directions, specified in Fig. 6.16, at the normal loads of 150 $\mu$N and 225 $\mu$N, respectively. It can be clearly observed that the pile-up increases with increasing normal load. Now, we shall do a slightly more detailed analysis by investigating any possible effect of the tip orientation and varying the normal load. At the same time we shall carry out a comparison with the results obtained from the MD simulations on the (100) surface of silver. Figs. 6.18, 6.19, and 6.20 show the top view of the scratches from both the experiments using the Triboscope and the MD simulations, when employing orientations (I), (II) and (III) of the
6.4 Comparison with Experimental Results

simulation indenter (or orientations (I)', (II)', and (III)' of the experimental

tip), respectively. Figs. 6.18, 6.19, and 6.20 also compare the scratches from
the Triboscope experiments at the two different loads of 150 and 225 µN. The shapes of the scratches, including the behaviour of the pile-up generated along
and at the end of the scratch grooves were found to be in very good agreement
with the MD simulations results.

The experimental results using the Triboscope are tabulated in Table 6.7. Fig. 6.21 explains some of the terminology employed in Table 6.7, for the differ-
ent pile-up generated during the scratching experiments. With the Triboscope
it has not been possible to measure the lateral forces during the scratching.
Therefore, the friction coefficient for this set of experiments could not be cal-
culated. The scratch hardness in the last column of Table 6.7 is calculated
as the ratio of the normal force and the square of the average scratch width.
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Figure 6.18: Top view of the substrate showing the scratch for the case of the (a) simulation performed using orientation (I) and at indentation depth of 10 Å, (b) experiment performed using the Triboscope and employing orientation (I)' at a load of 150 µN, (c) experiment performed using the Triboscope and employing orientation (I)' at a load of 225 µN.
Figure 6.19: Top view of the substrate showing the scratch for the case of the (a) simulation performed using orientation (II) and at indentation depth of 10 Å, (b) experiment performed using the Triboscope and employing orientation (II)' at a load of 150 μN, (c) experiment performed using the Triboscope and employing orientation (II)' at a load of 225 μN.
Figure 6.20: Top view of the substrate showing the scratch for the case of the (a) simulation performed using orientation (III) and at indentation depth of 10 Å. (b) experiment performed using the Triboscope and employing orientation (III)' at a load of 150 µN. (c) experiment performed using the Triboscope and employing orientation (III)' at a load of 225 µN.
6.4 Comparison with Experimental Results

Table 6.7: Results from the experimental investigations using the Triboscope on polycrystalline silver sample, and when employing the four orientations of the tip and at the two different normal forces.

<table>
<thead>
<tr>
<th>Tip Orientation</th>
<th>Average end pile-up (nm)</th>
<th>Average left pile-up (nm)</th>
<th>Average right pile-up (nm)</th>
<th>Length of scratch (µm)</th>
<th>Average scratch width (nm)</th>
<th>Scratch hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Normal load of 150 µN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I)'</td>
<td>43.0</td>
<td>14.6</td>
<td>8.5</td>
<td>4.0</td>
<td>422</td>
<td>0.8</td>
</tr>
<tr>
<td>(II)'</td>
<td>35.5</td>
<td>7.6</td>
<td>5.4</td>
<td>3.8</td>
<td>386</td>
<td>1.0</td>
</tr>
<tr>
<td>(III)'</td>
<td>23.4</td>
<td>6.4</td>
<td>17.9</td>
<td>3.4</td>
<td>363</td>
<td>1.1</td>
</tr>
<tr>
<td>(IV)'</td>
<td>25.2</td>
<td>20.9</td>
<td>14.1</td>
<td>3.5</td>
<td>328</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Normal load of 225 µN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I)'</td>
<td>59.0</td>
<td>51.8</td>
<td>8.7</td>
<td>3.7</td>
<td>680</td>
<td>0.5</td>
</tr>
<tr>
<td>(II)'</td>
<td>46.7</td>
<td>11.1</td>
<td>12.2</td>
<td>4.0</td>
<td>492</td>
<td>0.9</td>
</tr>
<tr>
<td>(III)'</td>
<td>50.7</td>
<td>4.8</td>
<td>19.7</td>
<td>3.8</td>
<td>563</td>
<td>0.7</td>
</tr>
<tr>
<td>(IV)'</td>
<td>27.0</td>
<td>23.4</td>
<td>14.0</td>
<td>3.8</td>
<td>540</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Similar to the MD simulations, the factor $k$ usually employed in the calculation of the scratch hardness (see Eq. 6.2) has not been considered in this experimental investigation. The scratch hardness was found to decrease with increasing normal load. The scratch width varies with the orientation of the tip but a direct dependence of the scratch width on the tip orientation can
hardly be considered because for the small indentation depth (at a normal load of 150 µN) the scratches have about the same widths (386 and 363 nm), when employing orientations (II)' and (III)', respectively, but this observation was not made for the case of the deeper scratches (at a normal load of 225 µN).

6.4.2 Experiments using the NanoScan

Two Ag samples were used for this particular experimental study:

(a) Sample A: Mechanically polished polycrystalline silver sample. The mean square roughness of the surface of this sample was more than 10 nm for the area of 6 x 6 µm². This value was certainly high and could have had an influence on the shape of the scratch. This problem was partially avoided by searching for the flatter areas of the surface.

(b) Sample B: Silver single crystal polished parallel to the (110) surface. It is a disc with diameter about 10 mm and 2 mm thickness and it has been polished using alumina and diamond. After that the sample has been treated by sputtering and annealing to remove the damaged layer and obtain a single crystal up to the surface. The mean square roughness became about 3 nm for the area of 6 x 6 µm².

The scratches on sample A were made at three different normal loads: 150, 225 and 300 µN. The scratches were carried out using the three indenter orientations (I)', (II)' and (III)', shown in Fig. 6.16, for each load. A further experiment was carried out on sample A at a normal load of 500 µN and using orientation (III)' of the tip. In addition, scratches were also made on the (110) surface of sample B at only two different normal loads: 150 and 225 µN, and the scratches were carried out using the three indenter orientations at each load.

In order to compare the scratches, an overview of the tip has been carried
6.4 Comparison with Experimental Results

out. Fig. 6.22(a) shows the indent on the silver surface and Fig. 6.22(b) shows

Figure 6.22: (a) 2D and (d) 3D image of an indent on the Ag surface using the NanoScan device. The load of the indentation is 2 mN. (c) Cross-section of the indent on the Ag surface. The direction of cross-section is shown by the line on the 2D image in (a).

the inverted 3D reconstructed image of the tip. The shape of the tip can be observed through the cross-section of the indentation image and this is shown in Fig. 6.22(c). The direction of cross-section is shown by the line on the 2D image in Fig. 6.22(a). The aspect ratio factor (width/depth) is approximately 10 and the vertex angle is approximately 150°. This factor has a great importance for comparing the experimental and simulated data, especially for the calculation of the hardness and frictional forces.
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Figs. 6.23(a)–6.23(f) show the scratches from both the experiments using the NanoScan device and from the MD simulations. Figs. 6.23(a), (c), and (e) are the results from the NanoScan experiments when employing tip orientations (I)', (II)' and (III)', respectively, at a scratching load of 225 µN on polycrystalline silver sample. Figures (b), (d) and (f) are the MD simulation results at an indentation depth of 10 Å on the (100) surface of Ag and using indenter orientations (I), (II) and (III), respectively.

Figure 6.23: Figures showing the scratches both from experiments using the NanoScan and the MD simulations. Figures (a), (c) and (e) are the results from experiments when employing tip orientations (I)', (II)' and (III)', respectively, at a scratching load of 225 µN on polycrystalline silver sample. Figures (b), (d) and (f) are the MD simulation results at an indentation depth of 10 Å on the (100) surface of Ag and using indenter orientations (I), (II) and (III), respectively.
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polycrystalline silver sample. Figs. 6.23(b), (d) and (f) are the MD simulation results at an indentation depth of 10 Å on the (100) surface of Ag and using indenter orientations (I), (II) and (III), respectively. The shapes of the scratches and the generation of the pile-up around the scratch grooves from the NanoScan experiments are, in general, very similar to those from the MD simulations.

Figure 6.24: Figures showing the scratches from the NanoScan experiments when employing orientation (I)' of the indenter at normal loads of (a) 150, (b) 225, and (c) 300 µN. The vertical scale of the images is in the range of 200–250 nm. A different behaviour of the pile-up generation for the lower load of 150 µN can clearly be seen. The light material refers to the pile-up above the sample surface and the dark material refers to the material below the surface.

Moreover, while the shapes of the scratches are in very good agreement with those from the MD simulations results, a different behaviour of the pile-up generation for the two different normal loads of 150 and 225 µN has been observed. Figs. 6.24(a)–6.24(c) show the different behaviour of the pile-up generation at the normal loads of 150, 225 and 300 µN, respectively, and when
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employing orientation (I)' of the indenter. This difference can be considered as a size-effect, which is common for this range of forces for silver. A significantly different behaviour of the pile-up generation for the lower load of 150 µN can clearly be observed from Fig. 6.24(a). Here, the substrate material is raked out mainly to the end of the scratch groove and generates one relatively big pile-up (refer to Fig. 6.24(a)). For the cases of 225 and 300 µN normal loads, the material was removed from the groove to the sides generating relatively smaller pile-up at the end of the scratch groove, and smallest pile-up on the right side of the groove and pile-up with intermediate height on the left side of the scratch groove.

On the other hand, the scratches on the (110) surface of sample B were found to have very similar shape and pile-up generation, compared to the results from the NanoScan experiments on the polycrystalline silver samples. Furthermore, the above-mentioned difference in the pile-up generation along the scratch groove for the loads of 150 and 225 µN was also observed.

The measured scratch widths, the pile-up generation and the scratch hardness, when employing sample A and sample B are tabulated in Tables 6.8 and 6.9, respectively. Table 6.8 shows that the scratch hardness decreases with increasing indenter load. This observation was also made from the experimental investigations using the Triboscope on the polycrystalline silver sample and from the MD simulations. However, there are nearly two orders of magnitude difference between the experimental results for the scratch hardness given in Tables 6.7 and 6.9 and the calculated scratch hardness from the MD simulations (Table 6.6). Scratch hardness and contact pressure are depth dependent concepts and this variation is probably due to the order of magnitude difference between the experimental scratch depths and those achievable by simulation.
### 6.4 Comparison with Experimental Results

Table 6.8: Results of the experimental investigations using the NanoScan device on polycrystalline silver samples, for the three tip orientations and at three different normal loads.

<table>
<thead>
<tr>
<th>Tip Orientation</th>
<th>Indentation depth (nm)</th>
<th>Scratch width (nm)</th>
<th>Maximum left pile-up (nm)</th>
<th>Maximum right pile-up (nm)</th>
<th>End pile-up (nm)</th>
<th>Scratch hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)'</td>
<td>31</td>
<td>300</td>
<td>11</td>
<td>9</td>
<td>104</td>
<td>1.67</td>
</tr>
<tr>
<td>(II)'</td>
<td>27</td>
<td>340</td>
<td>45</td>
<td>30</td>
<td>29</td>
<td>1.30</td>
</tr>
<tr>
<td>(III)'</td>
<td>33</td>
<td>493</td>
<td>26</td>
<td>18</td>
<td>12</td>
<td>0.62</td>
</tr>
<tr>
<td><strong>Normal load of 225 µN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I)'</td>
<td>51</td>
<td>440</td>
<td>36</td>
<td>14</td>
<td>120</td>
<td>1.16</td>
</tr>
<tr>
<td>(II)'</td>
<td>44</td>
<td>583</td>
<td>14</td>
<td>10</td>
<td>40</td>
<td>0.66</td>
</tr>
<tr>
<td>(III)'**</td>
<td>119</td>
<td>680</td>
<td>89</td>
<td>173</td>
<td>129</td>
<td>0.49</td>
</tr>
<tr>
<td><strong>Normal load of 300 µN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I)'</td>
<td>55</td>
<td>600</td>
<td>49</td>
<td>22</td>
<td>160</td>
<td>0.83</td>
</tr>
<tr>
<td>(II)'</td>
<td>87</td>
<td>720</td>
<td>57</td>
<td>64</td>
<td>184</td>
<td>0.58</td>
</tr>
<tr>
<td>(III)'</td>
<td>98</td>
<td>585</td>
<td>61</td>
<td>89</td>
<td>130</td>
<td>0.88</td>
</tr>
<tr>
<td>(III)'</td>
<td>87</td>
<td>800</td>
<td>86</td>
<td>15</td>
<td>150</td>
<td>0.78</td>
</tr>
</tbody>
</table>

** The scratch with load 225 has an exceptional size.

Table 6.9: Results of the experimental investigations using the NanoScan device on the (110) surface of single crystal silver sample, for the three tip orientations and at two different normal loads.

<table>
<thead>
<tr>
<th>Tip Orientation</th>
<th>Indentation depth (nm)</th>
<th>Scratch width (nm)</th>
<th>Maximum left pile-up (nm)</th>
<th>Maximum right pile-up (nm)</th>
<th>End pile-up (nm)</th>
<th>Scratch hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)'</td>
<td>33</td>
<td>670</td>
<td>50</td>
<td>37</td>
<td>62</td>
<td>0.33</td>
</tr>
<tr>
<td>(II)'</td>
<td>15</td>
<td>430</td>
<td>4</td>
<td>1</td>
<td>10</td>
<td>0.81</td>
</tr>
<tr>
<td>(III)'</td>
<td>32</td>
<td>586</td>
<td>37</td>
<td>21</td>
<td>10</td>
<td>0.44</td>
</tr>
<tr>
<td><strong>Normal load of 225 µN</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I)'</td>
<td>47</td>
<td>820</td>
<td>26</td>
<td>23</td>
<td>48</td>
<td>0.33</td>
</tr>
<tr>
<td>(II)'</td>
<td>34</td>
<td>663</td>
<td>35</td>
<td>14</td>
<td>41</td>
<td>0.51</td>
</tr>
<tr>
<td>(III)'</td>
<td>36</td>
<td>723</td>
<td>17</td>
<td>13</td>
<td>36</td>
<td>0.43</td>
</tr>
</tbody>
</table>
6.5 Conclusions

We have performed parallel MD simulations using atom decomposition of nanoindentation followed by nanoscratching on the silver (100) surface. We have studied the relation between the coefficient of friction, contact pressure, scratch hardness and the orientation of the indenter, which is a 90° triangular-based pyramid. Three different orientations of the indenter were considered. The tip orientation was found to have a significant effect on the friction coefficient. This was explained by the fact that the pile-up in front of the indenter is directly influenced by the indenter orientation and the pile-up in turn has an effect on the frictional force; because higher pile-up implies more resistance to motion. We, therefore, concluded that the shape of the tip has an effect on the friction coefficient.

Simulations were also performed for one of the indenter orientations at three different indentation depths of 5, 10 and 30 Å in order to investigate the behaviour of the friction coefficient and the hardness as a function of the depth. The friction coefficient was higher for the deeper indent of 10 and 30 Å compared to the friction coefficient for the shallow indent of 5 Å. Moreover, the scratch hardness decreases with increasing indentation depth and this was also observed by Komanduri et al. [46]. But to confirm this relation more simulations need to be run at varying depths.

The contact pressure is dependent on the tip orientation only for the shallow indent of 5 Å. In contrast the tip orientation has a significant effect on the scratch hardness at all depths. Both the contact pressure and the scratch hardness decreases as the indentation depth increases, but the contact pressure decreases more rapidly compared to the scratch hardness. The contact pressure and the scratch hardness have not yet reached a limiting value at the indentation depth of 30 Å; the maximum depth considered in the MD simulations.
6.5 Conclusions

Furthermore, an analysis of the local geometric configuration and potential energy of atoms underneath the tip shows that there are no dislocations generated in the shallow indent of 5 Å, but for the deeper indents, i.e., the one at a penetration depth of 10 and 30 Å we have observed the intersection of stacking faults on two \{111\} planes with each stacking fault being bounded by Shockley partial dislocations. These dislocations propagate in the (110) directions. Thus the formation of dislocations is dependent on the indentation depth, which explains why we have more dislocations at an indentation depth of 30 Å compared to the one at 10 Å and no dislocations for the shallow indent of 5 Å. This might explain the decrease in the scratch hardness as the indentation depth increases. The formation of dislocations was also found to be dependent on the indenter orientation.

Experimental investigations have also been carried out using two different devices: the NanoScan device, which is particularly designed for the scratching of hard materials and the Triboscope, specifically designed for nanoindentation experiments and thus scratching experiments were made through non-standard use of the device. These devices did not offer the capability to measure the lateral forces during the scratching experiments and as a result, the friction coefficient could not be calculated. The experiments were carried out for three different orientations of the indenter and at varying normal loads of 150, 225, 300 and 500 μN. When analysing the effect of the indenter orientation, the results obtained from the use of both devices were found to be in very good qualitative agreement with the results from the MD simulations. When investigating the effect of varying the normal load using the NanoScan device different behaviour of the pile-up generation was observed for the lower load of 150 μN compared to the other higher normal loads, this difference was associated to a size-effect. The scratch hardness was observed to decrease with increasing indenter load, when employing both the NanoScan and the
Results from the Steady-State Model

Triboscope, this trend was also seen in the results of the MD simulations.
Chapter 7

Results from the Spring Model

7.1 Introduction

In this chapter the spring model, with two coiled springs positioned in the horizontal ($x$) and vertical ($y$) directions, is employed to investigate the atomic-scale “stick-slip” phenomenon. The dynamics of the springs mimic the role of the AFM cantilever. The spring model provides us with some useful insight into the stick-slip phenomenon at the microscopic scale and an understanding of some of the important mechanisms that take place during stick and slip events. Scratch testing is an important practical tool for the investigation of surface mechanical properties and many MD studies of the stick-slip friction mechanism have been concerned with the study of sliding friction [54, 59, 107, 108]. However, in our investigation ploughing rather than sliding friction is considered. The dynamics of the indenter and the substrate, including the behaviour of the different forces in action, the coefficient of friction, and in particular stick and slip events are studied during scratching of an Ag(100) surface by an atomistic diamond tip. The effects of the sliding speed of the horizontal support and the indentation depth on the occurrence of the stick-slip events are investigated by considering sliding speeds between 1.0 and 5.0
Results from the Spring Model

ms$^{-1}$ and vertical support displacements of 5, 15 and 30 Å. Analysis of the local geometric configuration and potential energy of atoms underneath the tip is also performed to probe for any generation of subsurface defects.

7.2 Theory of the “Stick-Slip” Friction Mechanism

Stick-slip is a common phenomenon; for example, it is the cause of sound generation (a violin string, a squeaking door, or the chatter of machinery), sensory perception (taste, texture and feel), earthquakes, granular flow, and so on [36]. In any mechanism where the kinetic friction is less than the static friction there will be a tendency for the motion to be intermittent rather than smooth. The “stick” is due to the higher static friction between the surfaces, and the “slip” due to the lower kinetic friction during the slip itself [45]. The squeaks and grunts generated by sliding surfaces usually arise from vibrations set up by the intermittent nature of the sliding process itself. Intermittent motion is a common occurrence in sliding mechanisms and a great deal of ingenuity has been used in trying to overcome it, particularly in the operation of automated machinery. Because of the adverse effects of stick-slip, a number of methods are used to prevent it. These methods generally decrease the amplitude of the slip, or the sliding velocity during the slip, either by increased damping, increased inertia, or by increased stiffness of the spring [33].

The simplest model for explaining the stick-slip friction mechanism is the case of a spring with a mass attached to it on one end and a support attached to the other end, as shown in Fig. 7.1. In this setup the mass attached to the coiled spring is pulled by a tension force due to the support moving at a constant velocity $V_A$. The surface upon which this setup rests has a coefficient of kinetic friction that is much less than the coefficient of static friction. When
the spring is pulled one unit of distance, the tension is enough to overcome
the force of static friction, and the block begins to move. Because the kinetic
friction is far less than the static friction the block moves at a velocity faster
than that of the spring, rapidly restoring the spring to its unstretched length
causing the block to once again come to rest to start the entire process over
again. The block will again remain at rest until the tension exceeds the static
friction causing the block to move forward another unit of distance until the
mass stops because of the compression of the spring back to its unstretched
length. By performing this run at numerous support velocities and making
plots of position versus time, the trend we begin to see is that the faster the
support velocity, $V_A$, the less jerky the motion of the mass becomes. This can
clearly be observed in Figs. 7.2(a) and 7.2(b), where the velocity dependence
can easily be seen. Moreover, the motion of the mass becomes less jerky if the
two coefficients of friction (i.e. static and dynamic) approach the same value.

Despite the phenomenon of stick-slip occurring over any length scale [109] its origins are still not well understood. In macroscopic situations, Bowden and Tabor [45] attributed elastic deformation as a primary cause of stick-slip but it is not clear that this will also be the case for the microscale or nanoscale processes. Atomic-scale stick-slip in a scanning force microscope (SFM) was first reported by Mate et al. [25]. Stick-slip in an SFM can occur because the tip has to climb the potential hill of the surface atoms and thus is dependent on the direction in which the tip moves. A zig-zag motion of the SFM tip over
the surface can occur and for small sliding velocities a distortion of the SFM image is observed as the tip tries to keep to the lowest energy path [110].

Some recent studies have been carried out on sliding friction. One such investigation was performed by Riedo et al. [111]. The latter authors measured by means of an AFM the friction force between a silicon tip and a mica surface as a function of the externally applied force and velocity. They established the link between the friction force on a nanometre-sized tip sliding on a surface and the thermally activated hopping of the atoms in the contact on an effective interaction potential. On the other hand, Sang and co-workers [112] modelled friction acting on the tip of an AFM as it is dragged across a surface at non-zero temperatures and they found that the average frictional force is proportional to $|\ln v|^\frac{3}{2}$, where $v$ is the tip velocity. They also calculated the dependence of the average frictional force on both temperature and tip speed. Thus, for sliding friction, there has been shown to be a linear increase of the frictional force with the log of the sliding speed until a certain speed of around $0.5 \times 10^{-4}$ ms$^{-1}$ is reached at which point the frictional force remains approximately constant.
7.3 Details of the Simulation

[111, 112]. However, the simulations presented in this chapter are several orders of magnitude faster and are concerned with ploughing friction and so are not directly comparable.

Due to the fact that nanoscale stick-slip is an increasingly important phenomenon, a number of theoretical and experimental investigations have been carried out in recent years. Li et al. [107] performed molecular dynamics simulations of sliding friction showing that elastic deformation of the surface layers can be a cause of the atomic-scale stick-slip phenomenon. Landman and co-workers found atomic-scale stick and slip behaviour when shearing a Si tip on a Si(111) surface [113] and a CaF₂ tip on a CaF₂ substrate [49] by using molecular dynamics (MD) simulations. Sørensen et al. [59] performed MD simulations and observed a transition from smooth sliding with no static friction at low loads to atomic-scale stick-slip motion at larger loads. They found that larger loads also led to slip motion and plastic deformation of the tip. Other atomistic simulation work can be found in Refs. [59, 61, 108, 114, 115] and experimental work in, for example, Refs. [115]–[117]. A direct comparison between experiment and simulation is still not possible because of the differences between experimental time scales and system sizes and what is currently computationally possible with modern computational resources. However, despite differences between the speed of the tip and the size of the system, the simulations are able to capture many of the features observed experimentally.

7.3 Details of the Simulation

The simulations in this chapter are performed using the spring model (refer to chapter 5, section 5.5) and by employing orientation (III) of the indenter as shown in Fig. 6.1.
7.3.1 Speed of Nanoindentation and Nanoscratching

Simulations were carried out at an indentation depth of 5 Å and at three different sliding speeds of $V_A = 1.0, 2.5$ and $5.0 \text{ ms}^{-1}$, where $V_A$ is the sliding speed of the horizontal support A, shown in Fig. 5.5. The expected total horizontal distance covered by the indenter for the case of $V_A = 1.0 \text{ ms}^{-1}$ was 50 Å, whereas for the case of $V_A = 2.5$ and $5.0 \text{ ms}^{-1}$ it was 100 Å. Further simulations were performed at indentation depths of 15 and 30 Å and at a sliding speed of $V_A = 1.0 \text{ ms}^{-1}$ to study the effect of varying the indentation depth on the stick-slip events. For the simulations performed at indentation depth of 5 Å, the spring constants of the horizontal and vertical springs used in the calculations were $k_x = 40.05 \text{ Nm}^{-1}$ and $k_y = 240.30 \text{ Nm}^{-1}$ respectively, whereas for the simulation at the indentation depth of 15 Å the spring constants $k_x = 120.15 \text{ Nm}^{-1}$ and $k_y = 352.44 \text{ Nm}^{-1}$ were used. The values of the spring constants for the simulation at the deeper indent of 30 Å were $k_x = 368.46 \text{ Nm}^{-1}$ and $k_y = 560.70 \text{ Nm}^{-1}$. The mass of the tip was taken to be $3.14 \times 10^{-23} \text{ kg}$. The values of the vertical spring constants were chosen to be consistent with values in an SFM device and so that the actual scratch depth was between $\frac{1}{4}$ and $\frac{3}{4}$ the value of the support displacement. For nanoindentation devices the spring constants are typically larger than those used in the scanning force microscopy. A value of 560 Nm$^{-1}$ is towards the higher end of those quoted by instrument manufacturers. A similar reasoning was behind the choice of horizontal spring constant, i.e., the spring neither extended excessively during the dynamics nor was so stiff that it behaved as a solid body. If smaller values of the spring constants are used then the spring deforms further before the force builds up sufficiently for the motion to occur. However too large a value means that there is insufficient flexibility for the spring to extend or compress and the tip motion occurs as a forced motion moving with the prescribed velocity of the support.
7.3 Details of the Simulation

7.3.2 System Specifications

In the simulations, indenters of ~ 4100 and ~ 30,400 atoms are employed. Different substrate sizes are employed in the MD simulations, depending on the sliding speed and indentation depth in order to increase the efficiency in the use of the computing resources. The number of substrate atoms and the dimensions of the substrate that are employed in the different simulations are given in Table 7.1.

Table 7.1: Table showing the substrate sizes employed in the different MD simulations using the stick-slip model.

<table>
<thead>
<tr>
<th>Indentation Depth (Å)</th>
<th>Sliding speed of support A (ms(^{-1}))</th>
<th>Total simulation time (ns)</th>
<th>Dimensions of substrate (Å(^3))</th>
<th>Number of substrate atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.0</td>
<td>5.0</td>
<td>140 \times 20 \times 80</td>
<td>17,656</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>4.0</td>
<td>180 \times 20 \times 80</td>
<td>21,656</td>
</tr>
<tr>
<td>5</td>
<td>5.0</td>
<td>2.0</td>
<td>180 \times 20 \times 80</td>
<td>21,656</td>
</tr>
<tr>
<td>15</td>
<td>1.0</td>
<td>5.0</td>
<td>180 \times 45 \times 100</td>
<td>50,520</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>5.0</td>
<td>240 \times 80 \times 150</td>
<td>174,640</td>
</tr>
</tbody>
</table>

At the beginning of the indentation, the indenter vertex was positioned at a height of 5 Å above the substrate surface, which was outside the cut-off range of the tip-substrate interaction potential. The substrate was then indented to the required indentation depth. For the indentation depths of 5, 15 and 30 Å, the indenter apex undergoes total vertical displacements of only 6.25, 14.86 and 25.63 Å, respectively, due to the compression of the apex and the spring during indentation. Therefore, the actual indentation depths were 1.25, 9.86 and 20.63 Å for an indentation depth of 5, 15 and 30 Å, respectively.
7.4 Results

The results will be presented, by making first a comparison between the simulations performed at a fixed vertical support translation of 5 Å but at the three different sliding speeds of $V_A = 1.0$, 2.5 and 5.0 ms$^{-1}$; second, by comparing the results from simulations with the sliding speed of $V_A = 1.0$ ms$^{-1}$ but with different indentation depths of 5, 15 and 30 Å. Because the tip is modelled atomistically there is some distortion of the tip during both the indentation and the scratching process. For the nominal 5 Å indentation depth, the tip compresses by around 9% (2.4 Å in a tip height of 26.5 Å), which together with the spring compression gives an actual indentation depth of around 1.25 Å. During indentation the tip also undergoes a lateral distortion of 0.6 Å so that the vertex does not lie directly below the centre of mass of the top layer as it does at the start of the simulation. The distortion oscillates during the lateral motion, depending on the stick or slip event reaching a maximum of about 1.4 Å corresponding to a twist of $\approx 3^\circ$.

7.4.1 Effect of Sliding Speed

Figs. 7.3(a)–7.3(c) show the relationship between the horizontal spring force and horizontal displacement, for the three different sliding speeds of the support A. The spring force lies in the approximate range of 0–12 nN, for all the three cases. All the graphs have large maxima located at distances associated with the positions of atomic rows and corresponding to stick events. However, stick does not occur at all atomic rows, furthermore they show that slipping over atomic rows depends on the sliding speed. Micro-slip events can be seen at the beginning of the scratching simulations for the cases of $V_A = 2.5$ and 5.0 ms$^{-1}$, shown in Figs. 7.3(b) and 7.3(c). For these cases, at the start of the horizontal motion, there is no true stick and the small maxima in these curves
7.4 Results

Figure 7.3: Figures showing the plot of the horizontal spring force against the horizontal displacement of the indenter, for the three different sliding speeds of $V_A = 1.0$, $2.5$, and $5.0$ m/s at an indentation depth of 5 Å.

(a) $V_A = 1.0$ m/s

(b) $V_A = 2.5$ m/s

(c) $V_A = 5.0$ m/s
are due to the tip sliding over individual rows of substrate atoms (the Ag lattice constant is 4.09 Å), instead of ploughing through the substrate. There are also shoulders on the right slope of each peak which again correspond to the sliding of the tip over individual atomic rows.

Figure 7.4: Figures showing the emission of dislocations for the shallow indent of 5 Å and for a sliding speed of 1.0 ms\(^{-1}\). The figures are coloured according to the modulus of the slip vector given in the key.

The motion occurring after a major stick event was found to be associated with plastic deformation of the substrate with the emission of a dislocation
7.4 Results

Figure 7.5: Plots of (a) the horizontal displacement of the indenter and support A as a function of elapsed time; (b) the spring force in the horizontal direction and the vertical displacement of the fixed atoms of the indenter, against time at a sliding speed of 1.0 ms\(^{-1}\) and at an indentation depth of 5 Å. Here the zero point for the vertical displacement is after the indentation and relaxation phase.
in the region below the indenter. This is illustrated in Figs. 7.4(a)–7.4(f). Here, the atoms are represented as spheres, shaded according to the modulus of the slip vector [91]. The red atoms show the region of the lattice that have undergone a perfect dislocation, with Burgers' vector \( b = \frac{1}{2}(110) \), the green spheres represent atoms on a stacking fault. The emission of the dislocations occurs over a short time scale. At the end of the stick process shown in Fig. 7.4(b), a partial dislocation is emitted in the (10\( \bar{1} \)) direction followed by its retraction, Figs. 7.4(c)–7.4(e), and the emission of a full dislocation in the (10\( \bar{1} \)) direction. This then remains during the rest of the simulation. Figs. 7.4(b)–7.4(f) should also be compared with Figs. 7.5(a), 7.5(b) and 7.6. The stick event is clearly shown in Fig. 7.5(a) after 4.0 ns when the support and tip motion separates. There is even some motion of the indenter in the reverse horizontal direction until a catching up process occurs. The length of time of the stick event is quite short, of the order of 150 ps. During this time, Fig. 7.5(b) shows that there is an upward jump of the tip of about 0.5 Å as the stress in the substrate is relieved and the motion begins again. The horizontal spring force also begins to increase during the stick event. The

![Figure 7.6](image)

Figure 7.6: Figure showing the plot of the velocity of the indenter in the horizontal direction against the horizontal displacement of the indenter, for the case when the simulation was performed at a sliding speed of \( V_A = 1.0 \) ms\(^{-1} \) and at an indentation depth of 5 Å. The velocity is averaged over a time-scale of 25 ps.
emission of dislocations in the substrate was not observed for a 5 Å depth when the tip was constrained to move with a constant velocity, i.e. the simulations performed at an indentation depth of 5 Å employing the steady-state model (refer to Chapter 6). In that case only elastic deformation of the substrate took place. Here there is plastic deformation when the actual indentation depth is only 1.25 Å. Fig. 7.6 plots the velocity of the tip averaged over 25 ps time windows. There are a number of minima where the tip velocity is zero and even negative, corresponding to stick events and a clear slip event for the horizontal displacement of between 3 and 4 nm.

Fig. 7.7(a) shows the top view of the substrate surface at the end of the simulation showing the damage done to the surface by the indenter for a sliding speed of $V_A = 2.5 \text{ ms}^{-1}$. Fig. 7.7(b) shows the atoms underneath the substrate surface that have slipped. The scratch shown in Fig. 7.7(a) is not continuous compared to that seen when employing the steady-state model (refer to Chapter 6), where the top layer of the tip atoms were constrained to move in a pre-determined way without attached springs, because of the slip experienced by the indenter. It can be clearly seen that the initial motion occurs with such a slip event which is marked on the figure. This initial slip occurs also at a speed of 5.0 ms$^{-1}$. The jump over the surface corresponds exactly to the microslip events already discussed in the horizontal spring force plots of Fig. 7.3(b). A comparison between the surface damage of the substrate for the three cases where the simulations were performed at sliding speeds of $V_A = 1.0$, 2.5 and 5.0 ms$^{-1}$ shows that the surface damage is qualitatively the same in all three cases except for this initial slip which is more pronounced at the faster speeds. During this slip of the tip over the surface, Fig. 7.7(b) shows that no subsurface dislocations form. Dislocations are only formed in the substrate when stress is released after the next stick event. Fig. 7.7(a) also shows that there are few piled-up atoms on the surface despite the displacement.
of surface atoms to form the scratch. These atoms are displaced into the bulk through the dislocation emission process, there is a corresponding but small surface deformation.

Fig. 7.8(a) shows the variation of the coefficient of friction with horizontal displacement at a sliding speed of $V_A = 1.0$ ms$^{-1}$ and a vertical support displacement of 5 Å, which should be compared with the corresponding curve.

Figure 7.7: Figure showing the top view of substrate at the end of the scratching simulation, at the indentation depth of 5 Å and a sliding speed of 2.5 ms$^{-1}$. Figure (a) is coloured by depth, with light blue atoms above the surface and red atoms below the surface; (b) is coloured according to the modulus of the slip vector given in the key.
in Fig. 7.3(a). The stick events occur at distances of approximately 0.9, 1.5, 2.0 and 3.9 nm. At these events the coefficient of friction is reduced as the tip begins to accelerate. There are also some small peaks located at 3.2 and 3.6 nm during the slip process. Slip is easily recognised not only from the velocity curves but also as corresponding to that part of the curve in Fig. 7.8(a), where the friction coefficient has a low value. To get a better idea of the

Figure 7.8: (a) Plot of the friction coefficient against the horizontal displacement of the indenter, for the case when the simulation was performed at a sliding speed of $V_A = 1.0$ ms$^{-1}$ and at an indentation depth of 5 Å. (b) Same plot as in (a) in the domain $t = 2.0$ to $t = 3.2$ ns. $\mu$ increases to $\mu_s$ due to the build up in tension on the horizontal spring during the stick phase. The indenter slips and the kinetic component $\mu_k$ persists.
behaviour of the friction coefficient, \( \mu \), during one particular stick-slip event, in Fig. 7.8(b), we have split the graph in Fig. 7.8(a) and considered only the part from 2.0 to 3.2 ns. There is a stick event at approximately 2.4 nm where the value of \( \mu \) rises to the maximum value of the static coefficient of friction, \( \mu_s \). The vibrations in Fig. 7.8(b), which can be observed at a horizontal tip displacement of approximately 2.0 and 2.8 nm, is an artefact due to the effect of the springs in the model.

The actual values of static friction coefficient \( \mu_s \) given in Table 7.2 are an average of the largest peaks of the friction coefficient over the length of the scratch. The average normal and horizontal frictional forces and hence the dynamic friction coefficients for the three different sliding speeds and at the indentation depth of 5 Å are also calculated and the values are given in Table 7.2. Comparing the values of the static and dynamic friction coefficients at

Table 7.2: Results of the MD simulations for the three different sliding speeds and at an indentation depth of 5 Å.

<table>
<thead>
<tr>
<th>Sliding speed (ms(^{-1}))</th>
<th>Average normal force (nN)</th>
<th>Average frictional force (nN)</th>
<th>Dynamic friction coefficient ( (\mu_k) )</th>
<th>Static friction coefficient ( (\mu_s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>28.3</td>
<td>3.8</td>
<td>0.13</td>
<td>0.32</td>
</tr>
<tr>
<td>2.5</td>
<td>28.3</td>
<td>2.6</td>
<td>0.09</td>
<td>0.28</td>
</tr>
<tr>
<td>5.0</td>
<td>28.0</td>
<td>2.8</td>
<td>0.10</td>
<td>0.29</td>
</tr>
</tbody>
</table>

the indentation depth of 5 Å for the three different sliding speeds we can see that \( \mu_s \) takes a value of around 0.3, whereas the dynamic friction coefficient a value of around 0.1.

7.4.2 Effect of Indentation Depth

Figs. 7.9(a)- 7.9(c) compare the coefficient of friction for the three different indentation depths of 5, 15 and 30 Å. The maxima in Fig. 7.9(a) correspond
7.4 Results

Figure 7.9: Plots of the friction coefficient against the horizontal displacement of the indenter, at a sliding speed of 1.0 ms$^{-1}$ and at an indentation depth of (a) 5 Å, (b) 15 Å and (c) 30 Å.
Results from the Spring Model

Figure 7.10: A top view of substrate at the end of the scratching simulation at an indentation depth of 15 Å and a sliding speed of 1.0 ms$^{-1}$. Figure (a) is coloured on depth, where the light blue-coloured spheres around the edge of the hole represent piled-up atoms on the surface and red spheres represent subsurface atoms; Figure (b) is coloured according to the modulus of the slip vector. The slip planes on the substrate surface are marked by the white arrows in (a). The black arrow in (b) shows the dislocation underneath the scratch groove, which correspond to the slip plane in (a).
to the positions of atomic rows of atoms. The average normal and horizontal frictional forces and the dynamic and static friction coefficients at the three different indentation depths of 5, 15 and 30 Å and at a sliding speed of $V_A = 1.0 \text{ ms}^{-1}$ are calculated, and the values are given in Table 7.3. The dynamic friction coefficient at an indentation depth of 30 Å increases almost four times compared to the value obtained from the simulation performed at 5 Å. The static friction coefficient increases slightly less from 0.3 to 0.6. The value of the dynamic friction coefficient of 0.46 for the vertical support displacement of 15 Å, corresponding to an actual tip depth of 9.86 Å agrees almost exactly with the value of 0.41 previously calculated for an indenter constrained to move with a fixed speed at a depth of 10 Å (refer to Chapter 6). The actual values of the static friction coefficient $\mu_s$ given are an average of the largest peaks of the friction coefficient over the length of the scratch. As we indent deeper into the substrate, the static friction coefficient becomes indistinguishable from the dynamic friction coefficient, which can clearly be observed from Figs. 7.9(a)–7.9(c).

Table 7.3: The friction forces and coefficients at the three different indentation depths of 5, 15 and 30 Å, and at a sliding speed of $V_A = 1.0 \text{ ms}^{-1}$.

| Indentation Depth (Å) | Average Normal Force (nN) | Average Frictional Force (nN) | Dynamic friction coefficient ($\mu_k$) | Static friction coefficient ($\mu_s$) | $|\mu_s - \mu_k|$ |
|-----------------------|---------------------------|-------------------------------|--------------------------------------|------------------------------------|------------------|
| 5                     | 28.3                      | 3.8                           | 0.13                                 | 0.32                               | 0.19             |
| 15                    | 106.1                     | 49.1                          | 0.46                                 | 0.54                               | 0.08             |
| 30                    | 583.9                     | 332.8                         | 0.57                                 | 0.58                               | 0.01             |

Fig. 7.10(a) shows the surface damage for the simulation performed at indentation depth of 15 Å and at a sliding speed of 1.0 ms$^{-1}$. Here the maximum height of the pile-up of silver atoms is $\sim 7.9$ Å, compared to the case of the shallow indent where just a few adatoms were observed. The pile-
Figure 7.11: Graphs showing the horizontal displacement of the indenter and the horizontal support A, at a sliding speed of 1.0 ms$^{-1}$ and at indentation depths of (a) 5 Å, (b) 15 Å and (c) 30 Å.
Figure 7.12: Graphs showing the horizontal spring force against horizontal displacement of the indenter at a sliding speed of 1.0 ms$^{-1}$ and at indentation depths of (a) 5 Å, (b) 15 Å and (c) 30 Å, in the range of $t = 1.0$ to $t = 2.0$ ns.
Results from the Spring Model

up can also explain the higher static and dynamic friction coefficients for the case of the deeper indent, see Table 7.3, since the piled up material itself also acts as a resistance to the motion. This link between the pile-up and the friction coefficient was also observed in our investigation when employing the steady-state model (refer to Chapter 6). Fig. 7.10(a) also shows a continuous scratch with no slipping over the surface at this depth. Fig. 7.10(b) shows the corresponding sub-surface damage, which is also more evenly distributed than that for the shallower indent. At a particular slip event the indenter still displaces slightly in the negative y-direction but because the depth is greater, \(~9.86\,\text{Å}\), it continues to plough through the substrate instead of sliding over the surface as observed for the case of the shallow indent.

Figs. 7.11(a)–7.11(c) show the horizontal displacement of the indenter and the support A for the simulations at a sliding speed of 1.0 ms\(^{-1}\) and indentation depths of 5, 15 and 30 Å, respectively. For the 15 and 30 Å curves in Fig. 7.11(b) and Fig. 7.11(c), slip events can be observed where the horizontal displacement increases sharply but sticking occurs not by the tip coming to an actual halt as it did at 5 Å case, Fig. 7.5(a), but by the tip slowing to a speed which is less than that of the support, as seen by the smaller gradient of the indenter curve compared to the support curve.

Figs. 7.12(a)–7.12(c) compare the horizontal spring forces for the three scratching depths. The maxima in Fig. 7.12(a) corresponds to the positions of atomic rows of atoms. The spring force is approximately ten times higher for the indentation depth of 15 Å, Fig. 7.12(b), and almost thirty times higher for the indentation depth of 30 Å, Fig. 7.12(c), compared to that at 5 Å, Fig. 7.12(a). In addition, at the deeper depths (15 and 30 Å) there is no correspondence between the spring force maxima and the positions of atomic rows.
7.5 Conclusions

A spring model has been developed to investigate the atomic-scale stick-slip phenomenon for a pyramidal diamond tip in contact with the (100) surface of fcc silver. The MD simulations illustrate some important mechanisms that take place during stick-slip in this system. In particular they show that stick-slip is associated with the production of dislocations in the substrate below the indenter. Such dislocations were not observed at an equivalent indentation depth when dragging the tip at a constant speed and fixed depth (refer to the simulations employing the steady-state model in Chapter 6).

Varying the support sliding speed does not have an effect on the motion of the tip. At faster speeds the initial motion is such that the tip slides over the surface without sticking. Increasing the depth of the indenter gives a continuous line of damage to the substrate, and then stick-slip is manifested by periods of motion where the tip moves faster and then slower than the support (but does not come to a halt) and by the partly irregular shape of sides and bottom of the scratch.

For small vertical displacements the scratch in the substrate is not continuous, because the tip can jump over the surface when slipping, whereas at the deeper depths of 15 and 30 Å a continuous scratch is formed. The dynamic friction coefficient increases from $\sim 0.13$ to $\sim 0.57$ with increasing depth, but the static friction coefficient increases only from $\sim 0.32$ to $\sim 0.58$. Although the exact points of stick and slip depend on the sliding speed, the damage to the substrate, the atomistic stick-slip mechanisms, and the friction coefficients are relatively independent of speed over the range of values considered.

The dynamic coefficient of friction, which is an average value over the length of the scratch, calculated using the spring model is almost identical to that previously calculated with the steady-state model (simulations in Chapter 6) for the one case we have comparable data. However, the spring model
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allows the calculation of the static friction coefficient which was not possible previously. These static values are about three times larger than the dynamic values at a depth of 5 Å but lie closer to the dynamic values at the deeper depths of 15 and 30 Å, as might be expected because of the more uniform motion at the deeper ploughing depths.

The spring model has been successful in capturing the essential features of the stick-slip process during shallow surface scratching. Therefore, in the following chapter, we will investigate more complex systems where the effect of other parameters such as temperature and adhesion between surfaces are fully explored.
Chapter 8

Results from the Finite Temperature Model

8.1 Introduction

In this chapter, the finite temperature model, with three springs positioned in the horizontal ($x$), vertical ($y$) and lateral ($z$) directions, is employed to study the stick-slip phenomenon on materials with different crystal structures, i.e. fcc Ag, bcc Fe, and diamond Si. For the Si substrate, the effect of adhesive forces between the diamond tip and the substrate have also been investigated by simulating a hydrogen-terminated Si surface, which passivates the dangling bonds. Simulations are carried out at two different indentation depths of 5 and 15 Å to study the effect of indentation depth on stick-slip processes. In the previous chapter, we investigated the atomic-scale stick-slip phenomenon at low temperature with the motion of the tip constrained in lateral ($z$) direction. The simulations in this chapter are all carried out at a temperature of 300 K and the tip motion is also unconstrained in the $z$-direction.
8.2 Details of the Simulation

The simulations in this chapter are performed using the finite temperature model (see chapter 5, section 5.6 for more details on the model) and by employing orientation (III) of the indenter as illustrated in Fig. 6.1.

8.2.1 System Specifications

Simulations were carried out at indentation depths of 5 and 15 Å and at a sliding speed of $V_A = 1.0 \text{ ms}^{-1}$, where $V_A$ is the sliding speed of the horizontal support A (see Fig. 5.6). For the simulations performed at an indentation depth of 5 Å, the spring constants of the horizontal, vertical and lateral springs used in the calculations were $k_x = 40.05 \text{ Nm}^{-1}$, $k_y = 240.30 \text{ Nm}^{-1}$ and $k_z = 240.30 \text{ Nm}^{-1}$ respectively, whereas for the simulation at the deeper indent of 15 Å the spring constants were $k_x = 120.15 \text{ Nm}^{-1}$ and $k_y = k_z = 352.44 \text{ Nm}^{-1}$. The values of the spring constants were chosen to be consistent with values in an SFM device and also so that the springs did not elongate or compress excessively during a simulation.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Dimensions of substrate ($\text{Å}^3$)</th>
<th>Number of substrate atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>180 $\times$ 42 $\times$ 122</td>
<td>54,000</td>
</tr>
<tr>
<td>Fe</td>
<td>180 $\times$ 42 $\times$ 102</td>
<td>66,960</td>
</tr>
<tr>
<td>Si</td>
<td>180 $\times$ 42 $\times$ 102</td>
<td>43,520</td>
</tr>
<tr>
<td>H-terminated Si</td>
<td>180 $\times$ 42 $\times$ 102</td>
<td>44,880</td>
</tr>
</tbody>
</table>

In the simulations, a cube corner diamond indenter of $\sim 8400$ atoms is employed. The number of substrate atoms and the dimensions of the substrates that are employed in the simulations are given in Table 8.1.
8.3 Results and Discussions

The results will be presented, by first making a comparison between the simulations performed at the two indentation depths of 5 and 15 Å; secondly, by comparing the results from the simulations when employing the four different substrates. Thirdly, we will study whether constraining the indenter motion in the lateral (z) direction has any significant effect on the results obtained. Finally, we will investigate the effect of temperature by analysing the behaviour of dislocation emission from the simulations started at a temperature of 0 K and 300 K.

8.3.1 Effect of indentation depth

During the scratching, the indenter ploughs through the substrate resulting in the piling-up of substrate atoms in front of the indenter and along the sides of the scratch groove. The indentation depth determines the degree of pile-up in front of the indenter. The height of the pile-up in front of the indenter is given in Table 8.2 for the different substrates at the two indentation depths of 5 and 15 Å. As this pile-up increases there is more resistance to motion, therefore, a greater force is required to overcome this resistance which leads to an increase in the frictional force. It can clearly be observed that both the average normal and frictional forces (see Table 8.2) increase with the indentation depth. This in turn has a significant influence on both the dynamic and static friction coefficients. For the cases of the metals (Ag and Fe), both the dynamic and the static friction coefficients increase with increasing indentation depth, whereas the opposite behaviour is observed for Si. For the case of H-terminated Si the static friction coefficient decreases as the indentation depth increases but the dynamic friction coefficient increases. The reasons for the difference in behaviour for the Si cases might be because at the shallow depth there is
Results from the Finite Temperature Model

Figure 8.1: Figures showing the atoms adhered (encircled in black in (h)) to the indenter apex during the scratching simulation on Si at an indentation depth of 5 Å. The atoms are coloured on depth and the orange atoms represent the surface atoms.
8.3 Results and Discussions

Table 8.2: Results from the MD simulations, employing Ag, Fe, Si and H-terminated Si as substrates at indentation depths of 5 and 15 Å.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Normal force (nN)</th>
<th>Frictional force (nN)</th>
<th>Dynamic friction coefficient</th>
<th>Static friction coefficient</th>
<th>Height of pile-up (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>36.08</td>
<td>8.21</td>
<td>0.228</td>
<td>0.324</td>
<td>3.76</td>
</tr>
<tr>
<td>Fe</td>
<td>54.18</td>
<td>8.13</td>
<td>0.150</td>
<td>0.203</td>
<td>1.04</td>
</tr>
<tr>
<td>Si</td>
<td>21.71</td>
<td>43.98</td>
<td>2.026</td>
<td>2.520</td>
<td>4.11</td>
</tr>
<tr>
<td>H-terminated Si</td>
<td>22.53</td>
<td>25.74</td>
<td>1.142</td>
<td>1.688</td>
<td>2.63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Normal force (nN)</th>
<th>Frictional force (nN)</th>
<th>Dynamic friction coefficient</th>
<th>Static friction coefficient</th>
<th>Height of pile-up (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>106.29</td>
<td>43.20</td>
<td>0.406</td>
<td>0.500</td>
<td>9.00</td>
</tr>
<tr>
<td>Fe</td>
<td>160.88</td>
<td>64.96</td>
<td>0.404</td>
<td>0.450</td>
<td>8.94</td>
</tr>
<tr>
<td>Si</td>
<td>98.08</td>
<td>132.34</td>
<td>1.349</td>
<td>1.450</td>
<td>8.02</td>
</tr>
<tr>
<td>H-terminated Si</td>
<td>90.56</td>
<td>115.88</td>
<td>1.280</td>
<td>1.353</td>
<td>7.07</td>
</tr>
</tbody>
</table>

Resistance to motion due to adhesion between some of the Si atoms and the C atoms in the tip. Figs. 8.1(a)-8.1(h) illustrate the Si atoms that adhered to the indenter apex during the scratching simulation at a depth of 5 Å and were dragged along with the tip during the scratching. For the case of Ag (see Chapter 6), we observed that the pile-up generated during scratching was distributed along the scratch groove. However, here due to adhesion between the tip and the substrate atoms there are no atoms at the beginning of the scratch. The adatoms in Fig. 8.1(h) are those Si atoms that adhered to the tip apex and were dragged along during the scratching process.

As the depth increases the tip displacement through the substrate is more difficult because there is resistance to the motion from the atoms in front of the tip. Thus, at the deeper depth the resistance to motion due to the indentation depth becomes more important than the resistance due to adhesion. In addition, we can observe from Table 8.2 that Si and H-terminated Si have higher dynamic and static friction coefficients compared to those for the metals. Both the dynamic and static friction coefficients of Si are higher than the friction
coefficients for H-terminated Si, which would also indicate an adhesion effect, particularly because as the indentation depth increases both the dynamic and static friction coefficients were found to lie closer together. This is illustrated in Figs. 8.2(a) and 8.2(b).

![Friction coefficient as a function of horizontal displacement](image)

Figure 8.2: Plots of the friction coefficient as a function of the horizontal displacement of the indenter during the scratching simulation, for both Si and H-terminated Si substrates at indentation depths of (a) 5 Å and (b) 15 Å.

The difference between the static and dynamic friction coefficients, i.e. $|\mu_s - \mu_d|$, was found to decrease with depth and this could be explained by the argument that the slip events which can be observed where the horizontal displacement
of the tip increases sharply become less pronounced with increasing indentation depth (refer to Chapter 7). Hence, it becomes difficult to distinguish the static friction coefficient from the dynamic friction coefficient as the penetration depth increases. Moreover, for the case of Ag the value of the dynamic friction coefficient $\mu_k = 0.41$ for the vertical support displacement of 15 Å, corresponding to an actual tip depth of 10.7 Å, agrees with the value previously calculated (refer to the results from the steady-state model presented in Chapter 6) for an indenter constrained to move with a fixed speed at a depth of 10 Å. Also, the friction coefficients $\mu_k = 0.41$ and $\mu_s = 0.50$ are very similar to those obtained from the simulations at 0 K ($\mu_k = 0.46$ and $\mu_s = 0.54$, see Chapter 7).

8.3.2 Effect of substrate structure: Metals v/s Si v/s H-terminated Si

Table 8.3 shows that the tip compression during the indentation simulation on the Fe substrate is slightly larger than that for the other substrates, i.e. fcc Ag, Si and H-terminated Si, at both the indentation depths, 5 and 15 Å.

Two important parameters are calculated from the MD simulations and these are the contact pressure of the indenter on the substrate during indentation and the scratch hardness of the substrate during the scratching phase. The contact pressure sometimes referred to as nanohardness is defined as the ratio of the normal force and the contact area during indentation whereas the scratch hardness of the substrate is defined as the ratio of the average normal force during the scratching and the area supporting the indenter. The scratch hardness is calculated as an average of the contact pressure during the scratching process. The nanohardness and scratch hardness values for the different substrates employed in the simulations are given in Table 8.3. The contact pressure is higher than the scratch hardness for all the substrates, see Table
8.3. It is not clear that this trend will continue for deeper depths because it can be seen that at the deeper indentation depth the result is closer to the others than at the shallower depth.

Table 8.3: Results from the MD simulations, employing Ag, Fe, Si and H-terminated Si as substrates at indentation depths of 5 and 15 Å.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Actual indentation depth (Å)</th>
<th>Compression of the tip (Å)</th>
<th>Wear debris</th>
<th>Contact pressure (GPa)</th>
<th>Scratch hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Indentation Depth of 5 Å</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>2.345</td>
<td>1.202</td>
<td>89</td>
<td>41.914</td>
<td>35.584</td>
</tr>
<tr>
<td>Fe</td>
<td>1.035</td>
<td>1.971</td>
<td>62</td>
<td>144.543</td>
<td>67.972</td>
</tr>
<tr>
<td>Si</td>
<td>2.911</td>
<td>0.958</td>
<td>42</td>
<td>23.709</td>
<td>19.245</td>
</tr>
<tr>
<td>H-terminated Si</td>
<td>2.858</td>
<td>1.025</td>
<td>18</td>
<td>22.970</td>
<td>18.662</td>
</tr>
<tr>
<td><strong>Indentation Depth of 15 Å</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>10.663</td>
<td>1.256</td>
<td>792</td>
<td>24.096</td>
<td>18.842</td>
</tr>
<tr>
<td>Fe</td>
<td>8.843</td>
<td>1.766</td>
<td>589</td>
<td>50.247</td>
<td>34.567</td>
</tr>
<tr>
<td>Si</td>
<td>10.414</td>
<td>1.337</td>
<td>248</td>
<td>20.942</td>
<td>17.149</td>
</tr>
<tr>
<td>H-terminated Si</td>
<td>10.664</td>
<td>1.340</td>
<td>220</td>
<td>18.582</td>
<td>15.292</td>
</tr>
</tbody>
</table>

Figs. 8.3(a)–8.3(d) give a comparison between the scratches on the Ag, Fe, Si, and H-terminated Si substrates at an indentation depth of 15 Å, we can see that unlike the Ag and the Fe substrates, there is no pile-up at the beginning of the scratch for the case of Si and H-terminated Si. One possible explanation for this observation might be the dragging of the substrate material by the tip due to adhesion. Fig. 8.4(a) shows that at the beginning of the scratching simulations on Si and H-terminated Si at an indentation depth of 15 Å, the indenter undergoes a vertical displacement and thus indents further into the substrate, while it moves in the negative z-direction at the same time, Fig. 8.4(b). Figs. 8.4(a) and 8.4(b) show that there is a point during the scratching simulations, where the tip undergoes a maximum displacement in both the y and z directions. It is at this point that the indenter starts rising upward toward the substrate surface and it starts moving in the posi-
8.3 Results and Discussions

Figure 8.3: Top view of the substrate showing the surface damage at the end of the scratching simulation, when employing (a) Ag, (b) Fe, (c) Si and (d) H-terminated Si, as substrate at an indentation depth of 15 Å. The atoms are coloured on depth, where the spheres around the edge of the hole represent piled up atoms on the surface and the orange atoms represent the surface atoms. The arrows in (c) and (d) show the line of Si atoms attached to the rear of the indenter during adhesion and dragged behind the tip during the scratching process.
tive $z$-direction. Now if we look at the pile-up of the substrate atoms along the scratch grooves in Figs. 8.3(c) and 8.3(d), we can see that there is a line of atoms in the middle of the scratch, indicated by the dark arrows in the figures. These atoms are the Si substrate atoms located underneath the indenter before the indentation and scratching processes, which adhered to the tip apex during the indentation simulation. These atoms were then dragged along by the indenter during the horizontal displacement of the tip throughout.

Figure 8.4: Figure showing the plot of the (a) vertical ($y$) displacement of the indenter, (b) lateral ($z$) displacement of the indenter, (c) spring force in the $y$-direction and (d) spring force in the $z$-direction, as a function of the horizontal displacement of the tip during the scratching simulation, for both Si and H-terminated Si substrates at an indentation depth of 15 Å.
8.3 Results and Discussions

the scratching process.

The alternation between the stick and sliding states of the system reflects changes in the way energy is stored. While the system is stuck, elastic energy is stored in the system as potential energy due to work done by the horizontal support A. When the system slips this elastic energy is released as kinetic energy and eventually dissipated as heat. The system then sticks once more, begins to store elastic energy, and the process continues. Figs. 8.5(a)–8.5(h) illustrate the trend of the potential energy of the system during the scratching simulation at an indentation depth of 15 Å, when employing Ag, Fe, Si and H-terminated Si as substrates.

If we now concentrate on the simulation on Ag, see Figs. 8.5(a) and 8.5(b), we can observe that the build-up to the slip event corresponds to a gradual rise in the potential energy of the system. During this period the tip is said to be undergoing a stick event while the horizontal support continue on moving and thus the kinetic energy is converted into potential energy. This is also observed from Figs. 8.5(c) and 8.5(d) for the case of Fe. This gradual rise in the potential energy is then followed by a sudden drop, which corresponds to a slip event. This sudden drop in the potential energy occurs because during slipping, stress in the substrate is relieved, manifested in the form of dislocation emission underneath the scratch groove.

The dislocation emission is illustrated in Figs. 8.6(a)–8.6(f) and Figs. 8.7(a)–8.7(d) for Ag and Fe, respectively. Here the atoms are represented as spheres and are shaded according to the modulus of the slip vector [90, 91]. The red atoms show the region of the lattice that have undergone a perfect dislocation, whereas the green spheres represent atoms on a stacking fault. Figs. 8.6(a)–8.6(f) should also be compared to Fig. 8.5(a), where the slip events during the scratching simulation on Ag are indicated by the arrows. During the occurrence of the slip event around \( t = 1.0 \text{ ns} \) there is the emission of a first
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Figure 8.5: Figures (a), (c), (e) and (g) show the plot of the horizontal displacement of the indenter and the support A, when employing Ag, Fe, Si and H-terminated Si as substrate, respectively. The arrows point out the occurrence of the slip events. Figures (b), (d), (f) and (h) show the plot of the potential energy of the system against the horizontal displacement of the indenter when employing Ag, Fe, Si and H-terminated Si as substrate, respectively. The plots are from the simulations performed at an indentation depth of 15 Å.
8.3 Results and Discussions

Figure 8.6: Figures showing the emission of dislocations underneath the scratch groove during the scratching simulation on the silver substrate, at the indentation depth of 15 Å. The figures are coloured according to the modulus of the slip vector for Ag given in the key.
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Figure 8.7: Figures showing the top view of the subsurface damage underneath the scratch groove in the Fe substrate during the scratching simulation at an indentation depth of 15 Å. The atoms are coloured according to the modulus of the slip vector for Fe given in the key and the arrows point out the emission of dislocation.
8.3 Results and Discussions

Figure 8.8: Figures showing the subsurface damage underneath the scratch groove in the Fe substrate at an indentation depth of 15 Å and at $t = 1.5$ ns. Figure (a) is the top view and (b) is the side view of the Fe substrate, where the atoms are coloured on energy.

Dislocation, followed by the emission of a second dislocation and the retraction of the first one. Here, the red atoms show the region of the Ag lattice that have undergone a perfect dislocation, with Burgers' vector $\mathbf{b} = \frac{1}{2}(110)$. The green atoms designate those atoms that are on a stacking fault and the boundary in the plane of the fault, separating the faulted region from the perfect region of the Ag lattice, is a Shockley partial dislocation, with Burgers' vector $\mathbf{b} = \frac{1}{2}(112)$. Ag has a face-centred cubic (fcc) structure and as expected an fcc material slip is observed to occur on the $\{111\}$ planes with the slip direction being in the $(110)$ direction. Moreover, the emission and retraction of dislocation occurs over a very short time scale. For the case of Fe, comparing Figs. 8.7(a)–8.7(d) to Fig. 8.5(c) we can observe that the slip events are extrinsically linked to the dislocation emission underneath the scratch groove on the Fe substrate. The red atoms show the region of the Fe lattice that have undergone a perfect dislocation with Burgers' vector $\mathbf{b} = \frac{1}{2}(111)$; slip occurs in
the close-packed \{111\} directions in this bcc structure. The crystallographic slip planes are the \{110\} planes and these planes contain \langle111\rangle slip directions. The \frac{1}{2}\langle111\rangle dislocation splits into three \frac{1}{2}\langle111\rangle cores, but unlike the Shockley partial dislocations observed in fcc Ag these fractional dislocations do not bound stable stacking faults, which can clearly be observed from Figs. 8.7(a)–8.7(d). Figs. 8.8(a) and 8.8(b) show the same dislocation as in Fig. 8.7(a), except that here the atoms are coloured on energy. Figs. 8.9(a)–8.9(c) show the subsurface damage of the Fe substrate at an indentation depth of 15 Å and at the end of the scratching simulation.

Unlike the case of Ag and Fe, for the Si and H-terminated Si substrates slip events are not clearly discernible from the plot of the horizontal displacement of the tip against elapsed time of the scratching simulation, refer to Figs. 8.5(e) and 8.5(g). Analysis of the local geometric configuration and potential energy of the Si atoms underneath the tip shows that there are no sub-surface dislocations generated. However, we have observed that at the indentation depth of 15 Å some of the Si atoms have undergone a phase transformation instead, although no large-scale phase transformations have been seen at the depth considered in this investigation. Fig. 8.10 shows how the coordination number of some of the Si atoms changes during the indentation and scratching simulation at an indentation depth of 15 Å. There are now some Si atoms with coordination numbers between 5 and 8, with the majority of these being 5-fold or 6-fold coordinated. Here the atoms are coloured according to the coordination number, where the dark blue atoms are the Si atoms with a coordination number of 5 and the green atoms are those atoms with a coordination number of 6. The greenish-yellow and red atoms are those Si atoms with a coordination number of 7 and 8, respectively.

Figs. 8.5(f) and 8.5(h) show that for both Si and H-terminated Si there is a gradual increase in the potential energy during the scratching simulations,
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Figure 8.9: Figures showing the subsurface damage underneath the scratch groove in the Fe substrate at an indentation depth of 15 Å and at $t = 5.0$ ns. Figures (a) and (b) are the side view of the substrate and the atoms are coloured on energy and according to the modulus of the slip vector for Fe, respectively. Figure (c) is the lateral view of the substrate, where the atoms are coloured according to the modulus of the slip vector for Fe.
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except that at the beginning of the scratching simulation on Si, the potential energy undergoes a decrease first before it start increasing with the horizontal displacement of the tip. This might be explained by the fact that for the case of

\[ r > 42 \text{nm} \]

\[ (a) t = 0.07 \text{ ns} \]

\[ (a) t = 2.5 \text{ ns} \]

\[ (a) t = 5.0 \text{ ns} \]

Coordination number

\begin{tabular}{|c|c|c|c|}
\hline
5 & 6 & 7 & 8 \\
\hline
\end{tabular}

Figure 8.10: Figures showing the Si atoms that have undergone phase transformations during the indentation and scratching simulations, at an indentation depth of 15 Å. The atoms are coloured according to the coordination number and the colour scheme is given in the key.

Si there is adhesion between the Si atoms and the C atoms of the tip, whereas for the case of H-terminated Si there is less adsorption of the Si atoms to the indenter since any adhesion effect is counteracted by the hydrogen atoms on
8.3 Results and Discussions

the surface of the Si substrate. This decrease in the potential energy for the case of Si occurs because at the beginning of the scratching simulation some of the Si atoms undergo bond formation due to adhesion with the C atoms of the tip, i.e. the dangling bonds of some of the Si atoms reform with the other atoms so that all atoms retain approximately tetrahedral coordination. As scratching proceeds, bonds between some of the C atoms of the tip and the substrate atoms at the rear of the indenter are broken, while new bonds are formed between some of the C atoms and Si atoms in front of the indenter. Figs. 8.5(f) and 8.5(h) also show that the potential energy eventually rises for both Si and H-terminated Si. This increase in potential energy represents a phase change undergone by some of the Si atoms.

8.3.3 Effect of constraining the indenter motion in the z-direction

Figure 8.11: Figure showing the plot of the friction coefficient against the horizontal displacement of the indenter on the silver substrate during the scratching simulation, at an indentation depth of 5 Å, for the two cases where the spring in the z-direction was switched on and off.
Table 8.4: Results from the MD simulations employing Ag substrate at an indentation depth of 5 Å, for the case when the motion of the indenter is both constrained and unconstrained in the z-direction.

<table>
<thead>
<tr>
<th>z-spring</th>
<th>Normal force (nN)</th>
<th>Frictional force (nN)</th>
<th>Dynamic friction coefficient</th>
<th>Static friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>ON</td>
<td>36.08</td>
<td>8.21</td>
<td>0.228</td>
<td>0.314</td>
</tr>
<tr>
<td>OFF</td>
<td>35.04</td>
<td>9.80</td>
<td>0.280</td>
<td>0.373</td>
</tr>
</tbody>
</table>

Fig. 8.11 shows the behaviour of the friction coefficient as a function of the horizontal displacement of the indenter on the Ag substrate at an indentation depth of 5 Å, for the two different cases where the motion of the indenter was constrained and unconstrained in the z-direction. A slight difference is observed in the trend of the graph when the spring in the z-direction is switched on and off, what tends to justify constraining the motion in the z-direction in the earlier models. Table 8.4 shows that both the dynamic and the static friction coefficients were found to be slightly higher when the tip motion was constrained in the z-direction.

8.3.4 Effect of temperature: 0 K versus 300 K

The emission of dislocations in the simulations at 300 K were found to be associated with the slip events, and this was also observed in our previous simulations performed at 0 K (refer to Chapter 7). Figs. 8.12(a)–8.12(f) illustrate the dislocation emission process during the scratching simulation on the Ag substrate at an indentation depth of 5 Å. Figs. 8.12(a)–8.12(f) should also be compared with Figs. 8.13(a) and 8.13(b). The slip event that occurred at about $t = 3.4$ ns in Fig. 8.13(a) shown by the sudden increase in displacement correspond to the dislocations emitted in Figs. 8.12(c)–8.12(e). But unlike the simulations at 0 K in Chapter 7, here the dislocations are not full dislocations but rather partial dislocations and they are retracted just shortly after they
8.3 Results and Discussions

Figure 8.12: Figures showing the emission of dislocations underneath the scratch groove in the silver substrate, during the scratching simulation, for the shallow indent of 5 Å. The atoms are coloured according to the modulus of the slip vector for Ag given in the key and the arrows point out the emission of dislocation.
Results from the Finite Temperature Model

Figure 8.13: Plot of (a) the horizontal displacement of both the indenter and the horizontal support A, and (b) the horizontal spring force of the indenter, during the scratching simulation on the Ag substrate, at an indentation depth of 5 Å. The arrows in (a) indicate the occurrence of the slip events.
have been emitted, *i.e.* after the occurrence of the slip events, showing that the substrate is more malleable at a temperature of 300 K.

At a vertical support displacement of 5 Å (actual indentation depth ≈ 1.25 Å) the contact pressure and scratch hardness for Ag at 0 K are found to be 79.2 and 38.7 GPa, respectively, whereas when the support moves through a distance of 15 Å (actual indentation depth ≈ 9.86 Å) they are 26.9 and 19.6 GPa. These values are higher than the values obtained from the simulations on Ag at a higher temperature of 300 K: at a vertical support displacement of 5 Å the contact pressure and scratch hardness for Ag are found to be 41.9 and 35.6 GPa, respectively, whereas at a vertical support displacement of 15 Å they are 24.1 and 19.6 GPa. This is because the actual indentation depths are deeper at 300 K. The actual indentation depths at 300 K are 2.35 and 10.66 Å for specified vertical support displacements of 5 and 15 Å, respectively.

### 8.4 Experimental Results and Discussions

This section discusses the experimental investigations by our collaborators, Richter *et al.* [95, 118, 119] on single crystalline aluminium (Al), the (100) surface of Fe single crystal and untreated Si(100). The experiments by Richter *et al.* were performed using a HYSITRON Triboscope attached to a Nanoscope IV scanning force microscope. The Triboscope allows indentation tests to be performed with repeated loading and unloading [118]. These intelligent load functions result in multicycling indents at the same place on the sample surface. After loading, the force is decreased to about 20 % of the load maximum. This is done to avoid losing tip-to-sample contact. The sample is then reloaded to a maximum force, which is higher than that of the previous cycle. Multicycling testing enables experimentalists to obtain hardness and elastic modulus as depth dependent data.
8.4.1 Metals: Single crystalline Al and Fe(100) single crystals

The contact pressure (nanohardness) of most metals is depth dependent and there are three main regions that need to be considered. The first region is where the contact depth is less than 20 nm and here the hardness is mainly determined by elastic properties. This region is difficult to investigate due to surface roughness, blunting of the tip, soft contact and friction between the tip and the surface, which can cause relatively large errors. For larger penetrations, dislocations play an important role since we start to have plastic deformation. During the indentation process the tip induces the creation of dislocations [95] and this process is dependent on the size of the indent. In the region of about 20 to 400 nm contact depth, the hardness decreases and this is observed particularly for the case of metals (see Fig. 8.14(a) for the case of Al). When the penetration depth approaches a certain value the hardness is influenced by intrinsically existing dislocations in the materials. Around this zone of penetration depth the hardness reaches a plateau and is found to be no longer dependent on the contact depth. This is generally the expected constant hardness value for a material. This behaviour is seen in the depth dependent hardness curves for Fe(100) (Fig. 8.15) and other metals such as Al(100) (Fig. 8.14(a)).

Multi-indent experiments comprising of 7 cycles have been performed on single crystalline Al and Fig. 8.14(a) shows that the hardness for the Al sample decreases with increasing load. Now, since both Al and Ag have a fcc structure and have similar hardness values, we can do a comparison between the experiments on Al and the MD simulations on Ag. Fig. 8.14(b) shows the contact pressure as a function of indentation depth for the case when nanoindentation simulation was performed on Ag at an indentation depth of 15 Å. Comparing Fig. 8.14(a) and Fig. 8.14(b), we can observe that both graphs follow the same
Figure 8.14: (a) Graph showing the dependence of the hardness (contact pressure) on the contact depth, from the multicycling nanoindentation experiment on single crystalline Al. (b) The contact pressure as a function of the penetration depth from the MD simulation on Ag at an indentation depth of 15 Å.
Results from the Finite Temperature Model

trend. However, unlike the case of Al (Fig. 8.14(a)), Fig. 8.14(b) shows that the contact pressure for Ag has not yet reached a limiting value at the depth of 15 Å, maximum indentation depth considered in our MD simulations in this chapter.

The experimental observation of the nanohardness dependence on the contact pressure for the case of the metals agrees with the simulation results, where both the contact pressure and the scratch hardness were found to decrease with increasing indentation depth. This is shown in Table 8.3. The experiments show that as the indentation depth increases the contact pressure approaches a limiting value. The dependence of the nanohardness on depth for the case of the metals is also observed from the MD simulations on fcc Ag and bcc Fe, and the results agree with the experiments by Christopher et al. [94], where the nanohardness value of Ag and Fe is calculated to be $0.42 \pm 0.03$ and $1.9 \pm 0.1$ GPa at an indentation depth of 350 and 150 nm, respectively.

![Figure 8.15: Figure showing the contact pressure as a function of contact depth obtained from indentations with a cube-corner indenter with a load of up to 6000 µN on the (100) surface of Fe single crystal.](image)

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8.4 Experimental Results and Discussions

Furthermore, Fig. 8.15 shows the behaviour of the contact pressure as a function of contact depth measured from the nanoindentation experiment on the (100) surface of Fe single crystals. We can clearly observe that after a certain contact depth the contact pressure of Fe stabilises at a value of approximately 4 GPa. The contact pressure of Fe from the MD simulations was found to decrease from a value of 144.5 GPa at a depth of 5 Å to a value of 120
Results from the Finite Temperature Model

of 50.2 GPa at a depth of 15 Å.

The nanoindentation experiments on Al also demonstrates that the force curve is nearly linear, Fig. 8.16(a). This could be compared to the force-depth curve, Fig. 8.16(b), obtained from the simulation on Ag at an indentation depth of 15 Å. Since \( F \propto h^s \) (see Chapter 6, section 6.3.6), where \( F \) is the normal force, \( h \) is the indentation depth and \( s \) is a positive real number, the value of \( s \) can be calculated as the gradient of the line of best fit by plotting \( \log F \) against \( \log h \). This results in \( s = 1.2 \). When employing the model where no spring was involved during the nanoindentation process (steady-state model, Chapter 6) we found \( s = 1.7 \).

8.4.2 Untreated Si(100)

Due to the high hardness of some materials there is an extended depth region of pure elastic contact. At a particular depth the material starts to yield. The yielding for single crystals is often manifested by a pop-in, a sudden depth excursion due to nucleation and propagation of dislocations [119, 120]. Such a pop-in does not occur in all materials. If a material has several phases changing with pressure, the phase transformation limits the maximum pressure. Therefore, the hardness remains constant over a large range of load. Fig. 8.17 shows the displacement-force curve from the nanoindentation experiments on the (100) surface of untreated Si, which is an example of one such material. The multicycling indentation experiments on Si (unloading and reloading) illustrate hysteresis loops, which result from phase transformations.

From the experimental investigation Si was found to have a nearly constant hardness of 12.1 GPa. On the other hand, the MD simulations showed that the nanohardness and scratch hardness values of Si and H-terminated Si decrease less rapidly with increasing indentation depth, compared to the metals. As mentioned earlier, during indentation dislocations are either generated...
and/or set into motion. These defects change the hardness in dependence on

Figure 8.17: Force-displacement curve for the indentation experiment on untreated Si(100) surface for a multi-indent showing the unloading-reloading hysteresis loops.

the contact depth. Dislocations are easily created in metals, i.e. Ag and Fe, but it is harder to bring them into motion in semiconductors, for example Si. The energy to create dislocations in Si is higher than the energy for the phase transition, therefore hysteresis loops are found in the experiments (see Fig. 8.17). Si and superhard materials should not have depth dependent hardness properties, which is more or less what we can observe from the simulation results for Si in Table 8.3, where the contact pressure of Si at a depth of 5 and 15 Å are 23.7 and 20.9 GPa, respectively, and the contact pressure for H-terminated Si at a depth of 5 and 15 Å are 23.0 and 18.6 GPa. Thus, the value of the contact pressure reduces only slowly for Si as the depth increases compared to very large changes for metals. These values are still higher than
the experiment. If the trend in the slow reduction in calculated contact pressure with depth continues for Si, we would expect that the experimental value would be reached when the indentation depth is around 5 nm.

8.5 Conclusions

The model applied in this chapter is the most sophisticated that has been developed. It not only allows a study of temperature effects but also allows 3 degrees of freedom for the cantilever tip system. The model has been used to investigate the atomic-scale stick-slip phenomenon for a pyramidal diamond tip in contact with the (100) surface of both bcc and fcc (Fe and Ag) metals and semiconductors (Si). In order to study the effect of adhesion between the Si and C atoms of the tip further simulations were carried out by hydrogen-terminating the Si surface. Simulations were performed at two different support depths of 5 and 15 Å and at a temperature of 300 K. The temperature of the system was controlled via the Nose-Hoover thermostat.

The dynamic friction coefficient, which is an average value over the length of the scratch, calculated using the finite temperature model for Ag at the indentation depth of 15 Å is almost identical to that calculated with the steady-state model. In addition, the value of both the dynamic and the static friction coefficients of Ag agree almost exactly with those values obtained from the simulations with the 2-spring model at 0 K. Both Si and H-terminated Si were found to have higher dynamic and static friction coefficients compared to the values for the metals. However, both the dynamic and static friction coefficients of Si were higher compared to the friction coefficients for H-terminated Si, but the difference between the dynamic friction coefficient for Si and the one for H-terminated Si decreases with increasing indentation depth. This observation also holds for the static friction coefficient.
8.5 Conclusions

Experimental investigations have been carried out on the (100) surface of untreated Si, Al and Fe single crystals. Qualitative comparisons between the experimental measurements and the MD simulations are made where possible. We observed a qualitative agreement between the experimental and theoretical results.

The simulations with the finite temperature model also showed that for the case of the metals (Ag and Fe) stick-slip is associated with the production of dislocations in the substrate below the indenter and this observation was also made with the spring model for the investigations at 0 K. Unlike the 0 K simulations, the dislocations at 300 K are not full dislocations but rather partial dislocations and they are retracted shortly after the occurrence of the slip events. For the case of Si no dislocations are generated, instead some of the Si atoms undergo phase transformations, and the coordination number varies between 5 and 8, with the majority being 5-fold and 6-fold coordinated.

The constriction of the indenter motion in the lateral (z) direction was not found to have a significant influence on the dynamic and static friction coefficients compared to the friction coefficients values obtained when the indenter motion was left unconstrained in the lateral (z) direction.
Chapter 9

Final Conclusions and Future Work

Parallel MD simulations using both atom decomposition and spatial decomposition of nanoindentation followed by nanoscratching have been conducted on bcc Fe, fcc Ag, Si and H-terminated Si surfaces using a diamond indenter. The indenter was modelled atomistically and was a 90° triangular-based pyramid. The main objective of the study was to investigate the nanometre-scale ploughing friction and wear behaviour in order to gain insight into the different friction mechanisms and other events occurring on the atomic-scale. The behaviour of the friction coefficient, contact pressure and scratch hardness have been studied as a function of depth. The effect of the indenter orientation has also been analysed. The work material was observed to undergo both elastic and plastic deformation. In addition, the stick-slip phenomenon has been investigated both at a low temperature of 0 K and at room temperature (i.e. 300 K). The dynamics of the indenter and the substrate, including the behaviour of the different forces in action and the coefficient of friction, at particular stick and slip events have been studied. The variation of the sliding speed and indentation depth and their effects on the occurrence of the stick-slip events
has also been investigated.

The simulations showed that, for the case of the metals, stick-slip is associated with the production of dislocations in the substrate below the indenter. Furthermore, these dislocations were found to be full dislocations at the low temperature whereas at a temperature of 300 K they were more often found to be partial dislocations, that retracted shortly after the occurrence of the slip events. However, for the case of Si, analysis of the local geometric configuration and potential energy of the atoms underneath the tip showed that no dislocations were generated. Instead some of the Si atoms have been observed to undergo some local phase transformations.

Qualitative comparisons between experimental measurements and the MD simulations have been made where possible. The simulation investigations were constrained to systems that were comparatively smaller than those employed in the experiments. Hence, indentation depths and scratch lengths were typically one order of magnitude smaller than those in the experimental studies, while simulation times were several orders of magnitude shorter. Nevertheless, the simulations gave a good description of the nanoindentation and nanoscratching techniques and supported many of the experimental features.

The parallel MD code was initially developed to simulate nanoindentation [87, 93, 94, 95]. This code has been adapted to investigate friction on the atomic scale and the results are presented in this thesis. But nanotribology is such a vast field that we believe the nanofriction models employed in this thesis could be developed further to study and explore many other areas of nanotribology which are enumerated below.

In particular, sliding friction, which is one of the oldest problems in physics and certainly one of the most important from a practical point of view [32], could be studied with these methodologies in order to acquire a more comprehensive and general understanding of atomic-scale friction. Many studies have
been carried out on sliding friction [54, 59, 61, 107]. For example, Shimizu et al. [54] studied the atomic-scale stick-slip phenomenon during the sliding of rigid diamond on monocrystalline copper (Cu). The shortcomings of their model are that the interactions between the Cu atoms are modelled using the Morse potential [121], which is a pair potential. With our model, the interactions within fcc metals are modelled more realistically using many-body potential like, for example the Ackland’s EAM potential [78]. The EAM potential works well for close-packed solids such as Cu and Al.

Another shortcoming of Shimizu’s model [54] and the model employed by Bin Li et al. [107] is that their substrate size is comparatively small, i.e. 1600 atoms and 12,000 atoms, respectively. However, our model can easily simulate system sizes of 500,000 atoms and more. This is necessary to properly describe dislocations that are generated. In the work of Harrison et al. [61] they have considered sliding velocity of 50 and 100 ms\(^{-1}\), this is too fast and creates artifacts in the results. Our model allows us to employ a sliding velocity as slow as 1.0 ms\(^{-1}\) and simulation times as large as 5.0 ns.

Instead of investigating an indenter sliding on a substrate, the sliding friction studies could concentrate on the dynamics of two blocks of substrates in relative motion. We could, therefore, study the sliding of one solid body along another (e.g. metals and materials with diamond structures, such as Si) and investigate different conditions that directly have an impact on the friction coefficient.

Furthermore, our nanofriction model could also be developed to study lubrication, which is another branch of nanotribology. Thus, the effect of lubrication could be incorporated into the aforementioned study of sliding friction. One possible lubricant is hexadecane, which is an alkane. Hexadecane is a long chain hydrocarbon molecule composed of 16 carbon atoms that are fully saturated with hydrogen atoms. Its molecular formula is \(\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3\).
We chose hexadecane because it is a typical lubricant and since it contains C and H atoms so the interactions within the lubricant molecules could be modelled using Brenner's many-body potential [80, 81]. Carlson and Batista [122] performed some experiments to investigate the friction between two atomically smooth mica surfaces separated by an atomically thin layer of the molecules of the lubricant hexadecane. However, their main objective was to derive a constitutive relation that describe the frictional properties of boundary lubrication. Such a relation can provide some important guidelines for the design of mechanical systems, in terms of both materials choices and operating conditions. We could employ our model to evaluate the constitutive relation that they have proposed and at the same time concentrate on any effect of lubrication on the occurrence of stick-slip.

Bhushan et al. [123] studied the evolution of wear of a diamond-like carbon (DLC) coated disk substrate and their data illustrated how the microwear profile for a load of 20 µN develops as a function of the number of scanning cycles. Wear was initiated at the nanoscratches and so, nanoscratches and non-uniform coverage of DLC at nanoscratches acted as initiation sites, indicating that scratch-free surfaces were relatively resistant to wear. Similar studies could be performed using molecular dynamics simulations by employing the steady-state model (as discussed in section 5.4), by adjusting the period of scratching in order to perform multiple wear cycles. Simulations could be carried out on metals as well as on semiconductors. This would yield a better understanding on the factors linked to the generation of wear debris in different crystal structures, which in turn would provide an insight into approaches that may be adopted to minimise the wear rate.

One aspect of this thesis is that it is a component of a larger project that has been developed to study the amount of energy that is lost due to the friction generated between coal (carbon) and various materials during the
transportation process. All simulations in this thesis have been performed to investigate ploughing friction by employing a hard indenter (i.e. diamond) and both soft substrate (e.g. silver) and hard substrate (e.g. silicon). An interesting aspect that would be worth investigating is simulation with a soft tip instead and a hard substrate. However, the simulation of a soft tip on a hard substrate is not applicable to ploughing friction and hence we should concentrate on sliding friction. For example, the soft indenter could be made up of amorphous carbon, while the hard substrate could be diamond, silicon or metallic. This would give us an opportunity to investigate the same problem as King et al. [124] and correlate our results with their experimental results. From the MD simulations, a comparison could be made between the coefficient of friction and the hardness values for the two cases (i.e. hard tip-soft substrate and soft tip-hard substrate). In addition to this, for the hard tip-soft substrate case, plastic deformation of the substrate was observed and therefore, for the soft tip-hard substrate case we would expect deformation of the tip instead.

Moreover, the results from the simulations on silicon have shown that no dislocations were generated underneath the scratch groove (see Chapter 8). As a continuation to this work, it would be interesting to investigate the conditions under which we can have plastic deformation, including any generation of dislocations in silicon. And those conditions might include deeper indentation depths than those considered in this thesis and, possibly, higher temperatures. Another interesting effect that is worth investigating is the formation of cracks in silicon during scratching and any possible correlation between plastic deformation and crack formation.

In addition to this, further simulations could also be carried out with the finite temperature model but with the other two indenter orientations (I and II as shown in Fig. 6.1) that we did not consider in our investigations in Chapter 8. This would provide a perception into any possible effect of the indenter.
orientation on the occurrence of stick-slip.
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[88] The main LAM/MPI website is:
http://www.lam-mpi.org/

[89] Information on MPICH can be obtained at the following website:
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