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Molecular dynamics simulations of adhesion and nanoidentation of gallium arsenide

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MOLECULAR DYNAMICS SIMULATIONS OF
ADHESION AND NANOINDENTATION OF GALLIUM ARSENIDE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Physics and Astronomy

by
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# TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................... ii

LIST OF TABLES .................................................................................................................. vi

LIST OF FIGURES ................................................................................................................. vii

ABSTRACT ............................................................................................................................ xii

CHAPTER

1  INTRODUCTION ............................................................................................................... 1

2  NANOINDENTATION ....................................................................................................... 5
   2.1  Background .................................................................................................................. 5
   2.2  Measurement .............................................................................................................. 6
   2.3  Indentation size effect ............................................................................................... 9
   2.4  Simulation of nanoindentation .................................................................................. 12

3  MOLECULAR DYNAMICS .............................................................................................. 14
   3.1  The molecular dynamics method ............................................................................. 14
   3.2  Interatomic potentials for molecular dynamics ....................................................... 17
   3.3  Interatomic potential for GaAs ................................................................................. 20
   3.4  Measurement of physical properties ....................................................................... 22

4  NUMERICAL AND COMPUTATIONAL TECHNIQUES ........................................ 31
   4.1  Properties of integration algorithms ........................................................................ 31
   4.2  The Gear predictor-corrector algorithm .................................................................. 32
   4.3  Verlet integrators ..................................................................................................... 34
   4.4  Reference system propagator algorithms ................................................................ 35
   4.5  Short vs. long range forces ..................................................................................... 38
   4.6  Implementation of molecular dynamics
       on parallel computers ............................................................................................... 41
   4.7  Langevin dynamics .................................................................................................. 46

5  NANOINDENTATION SIMULATIONS ON GaAs FILMS ............................................ 47
   5.1  Treatment of the indenter ......................................................................................... 47
   5.2  Substrate construction and geometry ...................................................................... 51
   5.3  Load-displacement curves and mechanical properties ........................................... 54
   5.4  Analysis of pileup region ....................................................................................... 60
   5.5  Dislocation analysis ................................................................................................. 65
   5.6  Fracture of the substrate ......................................................................................... 71

6  INDENTER-SUBSTRATE ADHESION ............................................................................ 74
   6.1  Motivation and system construction ....................................................................... 74
   6.2  Load-displacement curves ...................................................................................... 77
6.3 Residual damage to the substrate .............................................. 82
6.4 Elastic recovery of the surface .................................................. 87

7 CONCLUSIONS AND FUTURE WORK ................................... 90
7.1 Conclusions ............................................................................... 90
7.2 Directions for future work ........................................................ 91

REFERENCES .............................................................................. 94

VITA .................................................................................................. 99
LIST OF TABLES

3.1 Parameters for Ga-As interaction. ................................................................. 22

5.1 Comparison of relative values for experimental microhardness and simulated nanohardness for gallium arsenide and silicon nitride. ............... 59

5.2 Elastic constants for GaAs at 300 K. ............................................................... 60
2.1 Schematic diagram of surface during and after nanoindentation. Note that substrate material deposited on the surface is suppressed for clarity in this figure. ................................................................. 7

2.2 Schematic of deformation bands underneath the indenter. The ratio of $d/d_m$ is the key parameter in one model of the indentation size effect. ................................................................. 11

3.1 The geometry of the Stillinger-Weber potential. Dark atoms represent equilibrium positions. The form of the potential imposes an energy penalty for deviations from the characteristic bond length and bond angle. The stiffness of the penalty is governed by the constants $B$ and $C$ in Equation 3.11. ...................................................... 20

4.1 Switching function ranges. The lighter blue region is the first region in Eqn. 4.23, where the forces are exclusively short range. The darker blue is the transition region, and the unshaded area is the region defined as long range. A cutoff distance is typically implemented, but is not illustrated here. ................................................................. 39

4.2 An MD system in two dimensions with the cell boundaries superimposed. The light blue overlay shows the area within the cutoff radius of the green atom. ................................................................. 40

4.3 (a.) For any atom in the dark blue central cell, only the atoms in the adjacent light blue cells must be searched for neighbors. (b) By building a neighbor list first, only half the adjacent cells must be searched. ................................................................. 41

4.4 Schematic of a typical distributed memory parallel computer. Portions of the simulated system are mapped on to each CPU and the network allow passing of atoms that cross domain boundaries to the CPU responsible for that domain. ................................................................. 42

4.5: Atoms adjacent to the domain boundary in neighboring domains are cached on the local processor. The small grid represents linked-cell boundaries, while the larger grid represents node boundaries. In this figure, the 16 linked cells shaded blue are cached on the node that they border. ................................................................. 44
4.6 Internode communication strategy for calculation of full pair correlation functions on eight nodes. The green boxes denote even-parity nodes, red denotes odd-parity nodes. The green arrows denote the first part of the message passing step, red arrows denote the second part of the message passing step. ........................................... 45

5.1 Flowchart illustrating the indenter update logic. This decision loop is not entered every timestep; rather, a parameter controlling the number of timesteps between each indenter update is passed to the program at the beginning of the simulation. At the end of this loop, the average x, y, and z components of the force are stored along with the center of mass of the indenter for this timestep, and the positions of the indenter atoms are updated. ................................. 49

5.2 Vickers indenter geometry. The offset is exaggerated for clarity. For microindentation, the specifications for the Vickers indenter have the offset width no more than 0.5 μm. ......................................................... 50

5.3 Schematic diagram of the GaAs system. ................................................................. 52

5.4 Indenter schedule. Note that the flowchart only depicts the loading half of the full traversal. Unloading was done by the same schedule depicted by the blue elements, from maximum load until the indenter reached its original position before the traversal. .............. 54

5.5 Load-displacement curve with continuous loading. ................................. 55

5.6 Load-displacement curve with holding phase. Compare the peak load to Figure 5.5. Also note that the curve overall is smoother. The smoothness is due to the averaging done at the end of each holding phase. ................................................................. 56

5.7 Schematic of determination of the length of the diagonal of the residual damage. The atoms shown are all atoms in the top few layers that fall within 1 Å in each direction from the indenter diagonal. ................................................................. 57

5.8 Illustration of pileup on the surface. The red atoms are pileup material, yellow atoms are surface atoms, and white atoms are indenter atoms. The view is perpendicular to one indenter face; the suppression of pileup along the indenter diagonals can be seen in the lack of pileup material at the edges of the faces. Picture courtesy of Andy Haas, NAVO Major Shared Resource Center, Stennis Space Center, MS. ................................................................. 61
5.9 Simulation schedule for preparing GaAs amorphous system. The system was determined to be melted when the plot of mean square displacement for atoms in the system drifted steadily upwards over time. 62

5.10 Bond length distribution comparison between the pileup material (red line) and bulk amorphous GaAs (blue line). 63

5.11 Bond angle distribution comparison. The red lines indicate data from the pileup region, the blue lines are bulk amorphous GaAs. The bond angle data indicate that the pileup material is structurally similar to the bulk amorphous GaAs system. 64

5.12 High-energy atoms underneath the indenter. Note the linear defect extending downward from the top surface. Green atoms are arsenic, red atoms are gallium. 65

5.13 Illustration of the centrosymmetry labelling on a simple cubic lattice. 67

5.14 Atoms with high centrosymmetry parameter. The linear defect observed in Figure 5.12 is not clearly highlighted here, illustrating the difficulty in differentiating the dislocation loops from the damage. All values of centrosymmetry parameter higher than 100 Å² were set equal to 100 Å² for clarity. Picture courtesy of Andy Haas, NAVO Major Shared Resource Center, Stennis Space Center, MS. 69

5.15 A z-plane slice at 20 Å below the substrate surface, illustrating the presence of dislocations. This image depicts a region 100 Å x 100 Å. Note that only As atoms are shown. Color indicates centrosymmetry parameter values. 70

5.16 Pressure distribution on a slice 20 Å below the surface of the GaAs substrate. No tensile wells that would indicate the presence of microcracking or pore formation are present. 72

5.17 Atomic positions on a slice 20 Å below the surface. Atoms are colored by their potential energy. For clarity, only arsenic atoms are shown. 73

6.1 The schedules for the adhesion simulations. The indenter velocity was the same 1 Å/ 500 pt rate described in Section 5.1. 76
6.2 Load-displacement relation for tip approach. The attractive well appears as the indenter atoms begin to interact with the surface, and disappears once the lowest layer of indenter atoms are close enough to the surface for the short range repulsion to dominate. .......... 78

6.3 Load-displacement curve for traversal to 7.5 Å depth. No hysteresis is observed. ................................................................. 79

6.4 Surface after 7.5 Å traversal. Note that while some atoms have been pulled from the surface, there is no residual damage in the system. This indicates that the surface damage was due solely to tip-surface bonding, as discussed in Section 6.4. Red atoms denote gallium, green atoms denote arsenic, and the indenter atoms have been removed for clarity. ................................................................. 80

6.5 Atomic positions (x,y) in the first subsurface layer underneath the indenter. Purple atoms are gallium, red atoms are arsenic. The lattice does not exhibit any residual damage from the indentation. .......... 81

6.6 Load-displacement relation for 18.3 Å traversal. A clear hysteresis is observed, indicating that the system has passed the yield point. The shoulder in the loading cycle occurring at a depth of about 8.5 Å is a candidate for the yield point, the point that marks the onset of plastic deformation. The peak load during this traversal is 1.25 μN. ................................................................. 82

6.7 Load-displacement relation after unloading from a depth of 8.5 Å. The red curves are the full 18.3Å traversal as shown in Figure 6.6, while the blue curve is the unloading curve from 8.5 Å. While the curve seems to retrace the loading curve for a portion of the unloading cycle, the indenter reaches the point of zero load before the indenter is fully withdrawn. The loading curve exhibits a slight anomaly in the data points just prior to the unloading, indicating the onset of plastic deformation. The yield point load is 0.6 μN. .......... 83

6.8 Top three layers of the substrate. Note the material that adhered to the indenter and was deposited on the surface, as well as the disruption in the definition of the layers. Purple atoms denote gallium, red atoms denote arsenic. The indenter atoms have been removed for clarity. ................................................................. 84
6.9(a) A (110) plane at a depth of 10 Å below the surface. Regions of plastic deformation consistent with the formation of dislocations highlighted. The region near the bottom of the image is located in roughly the same x-y position as a similar region in Figure 6.9(b). The 30 Å x 30 Å area that is the projection of the volume plotted in Figure 6.10 corresponds to the square that encloses the green circle highlighting the region. ................................................................. 85

6.9(b) A (110) plane at a depth of 18 Å below the surface. This the maximum depth the indenter reached during the traversal. Regions of deformation are highlighted. ................................................................. 85

6.9(c) A (110) plane at a depth of 28 Å below the surface. The damage in this plane is small compared to that shown in Figures 6.9 (a) and (b). .................................................................................................. 86

6.10 A projection onto the y-z plane of a 30 Å x 30 Å x 60 Å volume centered on a damaged region from Figures 6.9(a) and (b). The black line shows position of the surface and the blue lines are the positions of the slices for Figures 6.9(a), (b), and (c). ......................... 86

6.11 Substrate surface with the indenter at a depth of 7 Å. The view direction is along the \([\bar{1}10]\) direction. The indenter atoms have been removed to reveal the details of the surface. The center of the dimple is flat and remains relatively ordered, while the sloping regions at the edges of the dimple exhibit disordering. ....................... 87

6.12 Substrate surface after indenter withdrawal. While the surface has healed itself, three points along the surface exhibit pullout of surface atoms. These points correspond roughly to corners of the lowest plane of indenter atoms. Indenter atoms are shown in purple. Red atoms are gallium, green atoms are arsenic. ......................... 89
ABSTRACT

The purpose of this dissertation is to investigate the nanoscale hardness of gallium arsenide thin films and the elastic-plastic behavior of gallium arsenide under an indenter. These investigations were carried out using molecular dynamics (MD) simulations. The simulations are based on interatomic potentials that accurately reproduce many properties of bulk GaAs. The MD simulations performed required scalable and efficient algorithms for implementation on large parallel computers.

Nanoindentation simulations were performed using an ideal indenter that was held rigid during the simulation. To reduce the transient effects due to loading, the traversal of the indenter was interrupted periodically to allow the substrate to relax. Load-displacement curves were calculated and Vickers hardness and Young’s modulus were computed from the curves. The damage caused by the indenter was characterized in three ways. The material deposited on the surface was compared to bulk amorphous GaAs and found to be structurally similar, indicating that the material underwent solid-state amorphization under the indenter. Analysis of energetic atoms beneath the surface suggested the presence of dislocation loops. A centrosymmetry method was applied to characterize these defects. It was found that the method used did not perform adequately in the presence of amorphized material. Pressure distributions were calculated and atomic configurations were plotted to determine if subsurface microcracking due to the indentation was present. No indication of microcracking or pore formation was found.

Adhesion between the tip and substrate was also studied. The effect of the tip-surface attraction was studied for a modified Vickers indenter with a small flat surface instead of an atomically sharp tip. For indentations less than the yield point in GaAs, the
bond formation between the tip and the surface led to nonelastic deformation of the surface layer, while the layers undeneath the surface behaved in a purely elastic fashion. Through a series of small indenter traversals, the yield point of GaAs was determined to be 0.6 µN.
CHAPTER 1

INTRODUCTION

Since the introduction of the digital computer, scientists have been pushing the limits of that technology in order to enhance their ability to understand physical phenomena. Computer simulations are now widely accepted as a complementary method of investigation of certain types of physical problems. Advances in supercomputing have enabled the rapid growth in the utilization of these techniques [1].

Computer simulations are an important bridge between theoretical and experimental investigations. In order to be tractable, theoretical models are simplified by resorting to limiting assumptions. These assumptions often eliminate details from the model necessary for the theory to be compared in a meaningful fashion with experimental data. Experimental investigations also suffer from intrinsic limitations, including technological limitations as well as more fundamental limitations. It is often difficult or impossible to measure a single quantity or set of quantities that can be compared to a theoretical model. Computer simulations, while suffering from limitations of their own, can often bridge this gap.

Materials science and solid state physics cover a wide range of physical phenomena often with a high degree of complexity. Materials properties are affected by structures with a variety of length scales, from $10^{-10}$ to $10^{-2}$ meters and undergo dynamic processes with a range of time scales from $10^{-15}$ to $10^{7}$ seconds. Clearly, computer
simulations cannot fully describe such systems. They can, however, probe a range of length and time scales inaccessible to experiment.

The length and time scales available to computer simulations depend on the model used. In general, the level of detail that the model encompasses reduces both the number of atoms and the length of times that can be simulated. The extreme cases of this would be Kohn-Sham density-functional theory [2] where the electronic structure of the atoms simulated is calculated self-consistently, and finite element simulations [3], which are not atomistic at all, but instead treat small volumes of a solid within the elastic limit. A density-functional calculation can generally treat only on the order of 100 atoms, unless some further approximation is made, whereas finite element analysis is regularly used to model structures on the order of meters in size, containing many times $10^{23}$ atoms.

In this dissertation, we use classical molecular dynamics as the simulation technique. Classical molecular dynamics makes the assumption that a purely Newtonian description of atoms as indivisible force centers is sufficient to model most material behaviors. By doing so, we reduce the problem to one of $3N$ coupled ordinary differential equations, where $N$ is the number of atoms in the system. The dynamics in the system are a result of the atoms interacting with the interatomic potentials due to the other atoms in the system. These interaction potentials are empirical; they are parameterized representations fit to a variety of data, including the results of density-functional calculations in some cases.

By using this method, we are able to sample systems containing up to on the order of a billion atoms and time scales on the order of nanoseconds. While some materials
phenomena, notably fatigue and wear, are currently outside this range of time scales, many phenomena are more easily studied in this fashion than by experimental investigations. In this dissertation, we investigate the mechanical behavior of thin films under indentation. As the length scales of these films are on the order of a few nanometers, and the time scales necessary for a description of the indentation are on the order of hundreds of picoseconds, it is reasonable to use molecular dynamics as a tool in the investigation.

The keys to assuring the quality of the results are the quality of the interatomic potentials and the quality of the integration techniques used. Both of these are discussed in this dissertation, but it is important to note that, in general, a potential that gives an accurate representation of a bulk solid does not necessarily give an accurate representation of more complex configurations. It is therefore vital that we be able to validate against experimental data.

The choice of gallium arsenide was made due to the increasing importance of not only gallium arsenide itself, but also the wide range of III-V semiconductors. To be able to accurately predict the behavior of gallium arsenide would be a boon to researchers studying the behavior of nanoscale structures, including quantum dots. This choice also complements existing results on silicon nitride. Silicon nitride is used as the indenter tip material for commercial nanohardness testing equipment, and thus it is unlikely that meaningful comparisons with experimental data will become available. Gallium arsenide is significantly softer than silicon nitride and is of commercial importance. These factors make it likely that detailed nanohardness data will become available for comparison in the near future.
This dissertation is organized into seven chapters, the first of which is this introduction. Chapters discussing the relevant literature and background for nanoindentation (Chapter 2), molecular dynamics (Chapter 3), and numerical methods (Chapter 4) are included, followed by two chapters of results. Chapter 5 discusses the results from indentation simulations of a gallium arsenide film with an idealized indenter, while Chapter 6 discusses the results of small indents with adhesive interactions between the indenter and the substrate. A brief section summarizing these results and discussing directions for future work is included as Chapter 7.
CHAPTER 2

NANOINDENTATION

2.1 Background

Nanoindentation is a technique in which a nanometer scale indenter is used to damage a film. From this damage, measurements of the film’s resistance to plastic deformation can be made. This technique is used on both the micro and macro scales as well and has been well known on these scales for decades. In micro or macro scale indentation, a hard indenter, typically diamond, is used to damage the sample, and either an optical or electron microscope is used to image the damage area for measurement. For nanoscale indentation, an atomic force microscope tip is used.

The atomic force microscope (AFM) was developed by Gerd Binnig and collaborators at IBM as an application of the scanning-tunnelling microscope (STM) [4]. In its simplest form, the atomic force microscope consists of an atomically sharp tip attached to a cantilever arm. The cantilever arm sits on a piezoelectric cylinder. By lowering the tip to within a few angstroms of the surface of a sample, the force between the sample and tip can be measured by the piezo.

By using the piezo to force the tip into the sample, an indent can be made. Most atomic force microscopes, however, use lead zirconia titanate (PZT) piezos. These devices exhibit a considerable hysteresis effect making them unsuitable for measuring the force exerted during the indent [5]. Colton and co-workers adapted the typical AFM
device by replacing the PZT piezoelectric with lead magnesium niobate (PMN) electrostrictive actuators [5, 6].

2.2 Measurement

The primary measurement made in nanoindentation is the load-displacement curve. This plot shows the force required to push the indenter into the sample a certain distance. Load-displacement is a close analog to the more common engineering stress vs. strain curves encountered in materials testing. Features of typical interest on a load-displacement curve include the peak load, from which hardness is calculated, yield point, the point of onset of plastic deformation, and the compliance, which is the initial slope of the unloading portion of the curve.

Hardness is defined as the peak load divided by the projected area of the residual impression left by the indenter.

\[ H = \frac{F_{\text{max}}}{A} \]  

(2.1)

Hardness is measured in units of pressure and characterizes the ability of the material to resist plastic deformation [7]. It is not, however, solely dependent upon inelastic processes. The stress field due to the indentation may extend further into the sample than the damaged region [8].

To obtain the area of the residual impression in a nanoindent is more difficult than for a micro or macro scale indent. Direct imaging with the nanoindenter is often infeasible [5], and due to the size of the indent, the use of a second imaging instrument is also impossible. A calibrated indenter shape function, which gives the area of the indenter as a function of depth, is used instead [9].
This technique must take into account the fact that at peak load, the material is deformed both elastically and plastically. Simply using the shape function will yield a size somewhat larger than the residual indent. Instead, the projected area of contact with the indenter is used. This involves estimating the degree of elastic recovery [10, 11].

Figure 2.1 is a schematic diagram of the relevant quantities.

In Figure 2.1, \( h \) is the total indenter displacement, \( h_s \) is the displacement due to elastic deformation of the surface, which is completely recovered upon unloading, and \( h_c \) is the contact depth. When a shape function is used, \( h \) is clearly the incorrect value from which to calculate the projected area of contact. Instead, \( h_c \) should be used. Oliver and Pharr developed a relationship based on Sneddon’s analysis, which is discussed later, that allows \( h_s \), and thus \( h_c \), to be determined from the stiffness, or alternatively from \( h \) and \( h_f \), the residual depth of the indent [10].
The Young’s modulus of the material can also be estimated from the hardness data. Using a model based on elasticity theory for the deformation of an elastic half-space [12], Pharr and co-workers devised a relation between the Young’s modulus, the contact area, and contact stiffness [13]:

\[
\frac{dF}{dh} = S = \frac{2E}{\sqrt{\square} \left(1 - \nu^2\right)} \sqrt{A},
\]

where the left hand side is the slope of the initial portion of the unloading curve, \( A \) is the projected area of contact, \( E \) is the Young’s modulus and \( \nu \) is the Poisson ratio. The \( dF/dh \) term is commonly referred to as the stiffness, \( S \), of the material; its reciprocal is often termed compliance.

This analysis relies heavily on Sneddon’s analysis relating load, displacement, and contact area for any indenter consisting of a solid of revolution. Sneddon’s paper indicates that, in general, the relation between load and displacement can be described by the following form:

\[
F = \square h^m
\]

where \( F \) is the applied load, \( h \) is the displacement, and \( \square \) and \( m \) are constants [11].

In the case of a real indenter that also undergoes deformation, it has been proposed to replace the Young’s modulus in Equation 1.2 with a reduced modulus, \( E_r \), defined as

\[
\frac{1}{E_r} = \frac{(1 \square h^2)}{E} + \frac{(1 \square h^2)}{E_i}
\]

where \( E_i \) and \( \square \) are the modulus and Poisson’s ratio of the indenter. This expression is found in much of the relevant literature on nanoindentation and attempts to account for the indenter elasticity by simply including indenter and sample deformation in a single
term. Recently, it has been argued that in absence of an analytical solution for the
deformation of an elastic half-space by a non-rigid indenter, a better solution is to simply
make the assumption that the indenter is rigid [14]. This, of course, requires that the
Young’s modulus of the indenter be much larger than that of the substrate.

This model assumes that the initial slope of the unloading curve is linear. This is
the case where the indenter behaves in the same manner as a flat punch [13]. It has been
suggested that this model is insufficient to describe the unloading behavior of real
materials and that a power law fit based on the Sneddon result is more appropriate [10].
Recent simulation results [15] seem to indicate that a linear fit is sufficient in some cases.

The ratios of hardness to Young’s modulus are also of interest, given the
difficulty in calculating the projected area of contact. Joslin and Oliver [16] showed that
for simple rigid punches, the relation

\[
\frac{H}{E^2} = \frac{4}{\sqrt{S^2}}
\]  

(2.5)

where \( F \) is the applied load and \( S \) is the stiffness of the sample material, holds for a wide
variety of sample materials. This hardness to modulus ratio does not require any
knowledge of area function or projected area of contact.

2.3 Indentation size effect

One of the most intriguing results from experiment is an observed increase in
hardness as indent size decreases. This so-called indentation size effect (ISE) is typically
observed in brittle ceramics for indents smaller than 10-20 \( \mu \text{m} \) and for smaller indent
sizes in metals. The reported magnitude of the effect can be as high as three times the
hardness values on the macro scale [17]. Due to the size scales sampled with
nanoindentation, the ISE is of great concern.
Earliest explanations of the ISE were based upon microstructural considerations, assuming that the effect stemmed from the reduction of the indentation volume below the microstructural scale of the sample [18]. More recent explanations include the effects of statistical bias [19] on hardness measurements. The most commonly accepted explanation is by Bull, Page, and Yoffe, who have explained the size effect on the basis of the discretization of deformation in the sample [17].

This explanation assumes that as the indenter advances into the sample, that successive bands go through a cycle of elastic deformation followed by yielding and plastic deformation. As a band yields, the next band outward begins to deform elastically, and so forth. This can result in the measured length of the indenter diagonal, \( d_m \), being smaller than the diagonal length would be in an ideal material, \( d_i \). This discrepancy is assumed to be the source of the indentation size effect [17]. Figure 2.2 shows a schematic of this model.

Early quantitative models of indentation size effect used a simple empirical relation of the form

\[
H_m = qd_m^{n/2}, \tag{2.6}
\]

where \( H_m \) is the measured hardness, \( d_m \) is the measured indentation diagonal, \( q \) is a geometric factor, and \( n \) is the ISE index, a materials parameter. For \( n = 2 \), no indentation size effect is apparent. For most ceramics, \( n \) is less than 2. This simple formulation was fit to existing data and was unreliable for extrapolating behavior outside that data.
Using the model of discontinuous deformation described earlier, Bull and colleagues proposed a new quantitative model for the indentation size effect. By assuming that all growth in the measured indenter diagonal length must be by integral multiples of the width of the deformation bands, \( \delta \) (see Figure 2.2), they derived a relation of the form

\[
H_m = H_0 + \frac{d_i}{d_m},
\]

(2.7)
where $H_m$ is the measured hardness, $H_0$ is the ideal hardness, and $d_m$ is the measured indenter diagonal. This model proved to more accurately describe the ISE at very small length scales [17].

### 2.4 Simulation of nanoindentation

Simulations investigating the atomic-scale behavior in tip-substrate interactions have been being performed for over a decade. Previous theoretical descriptions of these interactions were based on elasticity and contact mechanics [20]. These formalisms are inadequate to explain the range of phenomena found in the tip-substrate interactions.

Landman and Luedtke investigated the so-called jump-to-contact phenomenon, a hysteresis in the load-displacement relationship occurring as the tip is first brought into the vicinity of the sample surface. Using molecular dynamics (MD) simulations with potentials based on the embedded atom method (EAM), the interaction between a gold tip and nickel substrate [20], and a nickel tip and gold substrate [21] were investigated. In both cases, it was found that atomic level instabilities contributed to the jump-to-contact phenomenon.

In the case of the nickel tip, it was found that the surface layers of gold jumped up to partially wet the tip. This adhesion formed a ductile neck that contributed to the load-displacement hysteresis [21]. Similarly, when a gold tip was used, it was found that the tip deformed to wet the Ni surface [20]. In both cases, the researchers attribute the onset of the instability and formation of the ductile neck to the system reaching a critical stress value.

A similar simulation was performed by Harrison et al. for a diamond indenter on a diamond surface [22]. In this simulation, Brenner’s empirical bond-order potential for
hydrocarbons [23] was used to model diamond. It was found that hysteresis was suppressed in simulations where the surface was passivated with a layer of hydrogen and the load was insufficient to plastically deform the surface. In other cases, Harrison and coworkers reported significant hysteresis in the load-displacement curves.

One issue with modelling diamond-on-diamond or, for that matter, any hard ceramic is that when the tip and indenter have similar or identical elastic moduli, certain calculations, including the derivation of Young’s modulus from the slope of the unloading curve, become difficult to perform reliably. Walsh and co-workers used an idealized fixed indenter to prevent this difficulty in a simulation of nanoindentation of silicon nitride [15]. Vickers hardness and Young’s modulus values were calculated for this system. The Young’s modulus value was within 10% of the value given by the interatomic potential used, and the hardness values compared well with the literature [24].
CHAPTER 3

MOLECULAR DYNAMICS

3.1 The molecular dynamics method

The molecular dynamics (MD) method involves solving a coupled set of differential equations under a variety of boundary conditions.

\[ \mathbf{f}_i = -\nabla V_r = m_i \ddot{r}_i. \]  \hspace{1cm} (3.1)

Equation 3.1 is easily recognizable as Newton’s equation of motion in its differential form.

A simulation using the MD method yields the phase-space trajectory, defined as the time evolution of the set of positions and momenta for the N particles. The numerical techniques for integrating the equations of motion, as well as the exact form of the equations themselves vary depending on the statistical ensemble for which the trajectory is computed. The ensembles are characterized by the thermodynamic variables that they conserve.

Most MD simulations are performed in either the microcanonical, or NVE, ensemble, which conserves the number of particles, N, the system volume, V, and the total energy, E, or the canonical, or NVT, ensemble, which conserves temperature, T, rather than energy. Another ensemble of interest is the isothermal-isobaric, or NPT, ensemble. The canonical ensemble is functionally equivalent to embedding the system in a heat bath; the NPT ensemble adds a mechanical coupling as well as a thermal coupling.
The equations of motion for these ensembles are best shown using a Hamiltonian formalism. Starting with a system of N classical, point-like atoms in a system of constant volume, we write the Hamiltonian as

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(\{r_i\}),$$  \hspace{1cm} (3.2)

where the $m_i$ are the particle masses, $p_i$ are the particle momenta, and $r_i$ are the particle positions. The Hamilton equations of motion are given by

$$r_i = \frac{\partial H}{\partial p_i}, \hspace{1cm} p_i = -\frac{\partial H}{\partial r_i}.$$  \hspace{1cm} (3.3)

Substituting Equation (3.2) into (3.3) recovers the Newton equations, (3.1). This Hamiltonian is valid for the microcanonical ensemble, and given a set of conservative forces, the total energy for the system will be conserved and equal to the Hamiltonian.

To derive equations of motions for other ensembles, additional terms must be added to the Hamiltonian to take into account the various additional degrees of freedom present. The Hamiltonian for the canonical ensemble was first derived by Nosé, [25, 26] and is given by

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i s^2} + V(\{r_i\}) + \frac{p_s^2}{2Q} + (3N + 1)k_B T \ln s,$$  \hspace{1cm} (3.4)

where $Q$ is the effective “mass” of variable $s$, which is interpreted as a time scaling factor, such that the simulation time $t' = t/s$, where $t$ is the time associated with the Hamiltonian in Equation 3.4. The variables $Q$ and $s$ thus describe the heat bath to which the system is coupled and when substituted into the Hamilton equations (3.3), will yield an equation of motion describing the time evolution of the heat bath. Hoover [27] later
derived a representation that was not dependent upon this time scaling and showed that Nosé’s equations of motion were unique, thus making the two representations equivalent.

The Nosé-Hoover dynamics for the canonical ensemble was extended by Martyna et al. to describe a chain of coupled thermostats [28]. This is equivalent to embedding the coupled system consisting of the microcanonical system and its coupled heat bath inside another heat bath, and so on. The Hamiltonian for this extended heat-bath is given by

$$\hat{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(\{r_i\}) + \sum_{i=1}^{M} \frac{P_\Omega^2}{2Q_i} + Nk_B T \sum_{i=2}^{M} \hat{\Omega}_i + k_B T \sum_{i=2}^{M} \hat{\Omega}_i,$$

(3.5)

where $M$ is the number of thermostats, $\Omega_i$ and $\hat{\Omega}_i$ and $P_\Omega$ are the mass and momenta respectively of the thermostat $\Omega_i$. The advantage of this formalism is that it yields correct canonical distributions of positions and momenta for very small or very stiff systems, which Nosé-Hoover dynamics do not [28].

Constant pressure simulations add a mechanical coupling to the system instead of a thermal coupling such as a heat bath. The original method due to Andersen [29] created a “pressure bath” variable in much the same fashion as Nosé’s heat bath variable. Parrinello and Rahman [30, 31] later generalized this technique by allowing not only the volume, but also the shape of the MD box to vary. This yielded a method quite suitable for studying phase transitions in crystals. By defining a matrix

$$\mathbf{H} = \{h_1, h_2, h_3\}$$

(3.6)

whose columns are vectors defining the three axes of the MD simulation box, a set of dynamic variables describing the time evolution of this matrix can be computed along with the trajectory of the particles within it.
The equations of motion for this ensemble are generated by adding terms to the equations of motion for the NVT ensemble from the Hamiltonian in Equation 3.6 to account for the kinetic and potential energies of the box. Following Martyna et al. [32], the equations of motion are

\[
\dot{r}_i = \frac{p_i}{m_i} + \frac{P_g}{W_g} r_i
\]

\[
\dot{p}_i = F_i - \frac{P_g}{W_g} p_i - \frac{1}{3N} \frac{\text{Tr}[P_g]}{W_g} p_i - \frac{p^2_i}{3} + \frac{k_B T}{N} \frac{p_i}{m_i}
\]

\[
\dot{\hat{H}} = \frac{P_g H}{W_g}
\]

\[
\dot{\hat{P}}_g = V(P_{\text{int}} \hat{I} P_{\text{ext}}) + \frac{1}{3N} \sum_{i=1}^{N} \frac{p^2_i}{m_i} + \frac{k_B T}{N} \text{Tr} \left[ \hat{P}_g \hat{P}_g \right] - \frac{3}{2} \left( 3N + 9 \right) k_B T
\]

where $P_g$ and $W_g$ are the box momentum and mass, $P_{\hat{g}}$ and $Q$ are the momentum and mass associated with the thermostat, $P_{\text{int}}$ and $P_{\text{ext}}$ are the internal and external (applied) pressures respectively, and $\hat{I}$ is the identity matrix.

These equations, since they place no constraints upon the cell matrix, can lead to a general rotation of the simulation space. This complicates data analysis immensely. This rotation can be avoided by using a symmetrized cell momentum tensor. This approach is implemented by constraining $g = \tilde{g}$, where $P_g = W_g$ [32].

### 3.2 Interatomic potentials for molecular dynamics

The interatomic potentials used for MD are the key to reproducing the physical properties of the materials simulated. The generalized interatomic potential can be
formulated in terms of one-body effects, two-body or pair effects, and so on to higher orders and can be written thus:

\[ V = \sum_i V^{(1)}(r_i) + \sum_{j \neq i} V^{(2)}(r_{ij}) + \sum_{k \neq j \neq i} V^{(3)}(r_{ij}, r_{ik}) + \cdots, \tag{3.8} \]

where \( r_{ij} \) is the separation between atoms \( i \) and \( j \). One-body terms represent the potential energy of atoms in an external field and are typically not important in MD simulations. Two-body terms are pair interactions, including Coulomb and van der Waals forces, and are the simplest and most commonly used potentials. Potentials consisting solely of two-body terms have had remarkable success reproducing the properties of some realistic systems. Three-body terms are necessary, however, to accurately represent strongly covalent crystals, as bond angle constraints are difficult to represent otherwise.

One of the simplest realistic potentials is the Lennard-Jones 12-6 potential, given by

\[ V(r_{ij}) = 4\varepsilon \left( \left( \frac{r_0}{r_{ij}} \right)^{12} - \left( \frac{r_0}{r_{ij}} \right)^6 \right). \tag{3.9} \]

This potential generates a steep repulsion as the atoms move closer than some equilibrium distance \( r_0 = 2^{1/6} \varepsilon \) and an attractive well for \( r > r_0 \). This simple potential is well suited for simulating systems of inert gases. This potential has the advantage of being short-ranged; the potential quickly falls to negligible values for large values of \( r \) and can thus be cut off at a certain distance without significantly affecting the behavior of atoms in the potential. The effect of this short-rangedness is that the number of atoms to consider in calculating the force on an single atom is small compared to the total number of atoms in the system.
Contrast the behavior of the Lennard-Jones potential to potentials such as the Coulomb potential, which is given by

\[ V(r_{ij}) = \frac{Z_i Z_j}{r_{ij}}. \]  

To calculate the effect of the Coulomb potential on a single atom requires that every other atom in the system be taken into account, thus making the force calculation scale as the square of the number of atoms in the system. It is not feasible to make large-scale computations with this limitation. The simplest approximate method of reducing this \( N^2 \) scaling to scaling linearly with the number of atoms in the system is by introducing a screening term, which allows the Coulomb potential to fall off smoothly at large distances at the cost of neglecting far field effects. Another more exact method is the Fast Multipole Method (FMM) developed by Greengard and Rokhlin [33], which allows far-field effects to be represented by a multipole expansion.

A common three-body potential form is that of the Stillinger-Weber potential. Stillinger and Weber [34] pointed out that pair potentials were inadequate for describing diamond lattice structures and proposed a three-body potential of the form

\[ V_{\text{Stillinger-Weber}} = B \exp \left( \frac{C}{r_{ij} - a} \right) + C \exp \left( \frac{C}{r_{ik} - a} \right) \left( \cos \theta_{ijk} - \cos \theta_{ijk} \right)^2, \]  

where \( a \) is the cutoff distance, and \( B \) and \( C \) are constants. The exponential terms reflect the effects of bond stretching, placing an energy penalty on deviation from some characteristic length. Figure 3.1 illustrates the geometry of the Stillinger-Weber potential.

Bond order potentials are a class of interatomic potentials that do not fit into the strict formalism described by Equation 3.8. Instead, they allow the bond strength to
Figure 3.1: The geometry of the Stillinger-Weber potential. Dark atoms represent equilibrium positions. The form of the potential imposes an energy penalty for deviations from the characteristic bond length and bond angle. The stiffness of the penalty is governed by the constants $B$ and $C$ in Equation 3.11.

vary based on local coordination. As such, they are well suited for modelling hydrocarbon chains, where the nature of the carbon-carbon bond changes on the basis of the local environment. This allows the differences between the carbon single, double, and triple bonds to be accurately modelled. The most widely applicable and commonly used bond-order potential is the Reactive Empirical Bond Order (REBO) potential developed by Brenner [23]. The bond-order potential formalism was originally developed by Abell, who derived a general expression for binding energy based on the local environment [35], and Tersoff, who introduced analytical potential energy functions based on Abell’s work [36, 37].

3.3 Interatomic potential for GaAs

In simulations described in Chapters 4 and 5, the interatomic potentials were developed by Vashishta et al. [38] to describe gallium arsenide. This potential contains both two and three body terms, and has the form
\[ V = \sum_{j \neq i} \psi_{ij}^{(2)}(r_{ij}) + \sum_{k \neq j, i} \psi_{ijk}^{(3)}(r_{ij}, r_{ik}) \]

\[
\psi_{ij}^{(2)} = \frac{H_{ij}}{r_{ij}^{d}} + \frac{Z_i Z_j}{r} \exp\left(\frac{-r}{r_{iv}}\right) + \frac{D_{ij}}{r^4} \exp\left(\frac{-r}{r_{4s}}\right) + \frac{W_{ij}}{r^6}
\]

\[
\psi_{ijk}^{(3)} = B_{ijk} \exp\left(\frac{-r_{ij} - r_{ik}}{r_0}\right) + \frac{1}{2} \cos(\xi_{ijk} \xi_{ijk})^2
\]

\[ \text{where} \]

\[
H_{ij} = A_{ij}(\xi_{i} + \xi_{j})^{d}
\]

\[
D_{ij} = \frac{1}{2}(\xi_{j}Z_i^2 + \xi_{i}Z_j^2)
\]

The first term of the second line of Equation 3.12 describes the steric repulsion, the second term is a Coulomb term with an exponential screening factor, the third term is a screened charge-dipole interaction, and the last term describes van der Waals interactions between atom pairs. The third line in the equation is clearly a three-body term of the Stillinger-Weber form.

The parameters in this potential were fitted to reproduce experimental values for GaAs, including lattice constant, cohesive energy, and elastic constants for the crystalline phase. The potential gives a good description of melting temperature, fracture energy, and phonon density of states. The potential also gives good agreement with experimental X-ray static structure factor of amorphous GaAs. Additionally, a high-pressure phase transition from zinc-blende (4-fold coordination) to rocksalt (6-fold coordination) is also correctly described [38]. The values for the potential parameters used are given in Table 3.1.
Table 3.1. Parameters for Ga-As Interaction

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{Ga-Ga}}$</td>
<td>$16.4984 \times 10^{-19}$ J</td>
</tr>
<tr>
<td>$A_{\text{As-As}}$</td>
<td>$2.0623 \times 10^{-19}$ J</td>
</tr>
<tr>
<td>$A_{\text{Ga-As}}$</td>
<td>$2.0623 \times 10^{-19}$ J</td>
</tr>
<tr>
<td>$\theta_{\text{Ga}}$</td>
<td>$0.95$ Å</td>
</tr>
<tr>
<td>$\theta_{\text{As}}$</td>
<td>$1.498$ Å</td>
</tr>
<tr>
<td>$\theta_{\text{Ga-Ga}}$</td>
<td>$7$</td>
</tr>
<tr>
<td>$\theta_{\text{As-As}}$</td>
<td>$7$</td>
</tr>
<tr>
<td>$\theta_{\text{Ga-As}}$</td>
<td>$9$</td>
</tr>
<tr>
<td>$Z_{\text{Ga}}$</td>
<td>$0.9418$ e</td>
</tr>
<tr>
<td>$Z_{\text{As}}$</td>
<td>$-0.9418$ e</td>
</tr>
<tr>
<td>$\theta_{\text{Ga}}$</td>
<td>$0.0$ Å$^3$</td>
</tr>
<tr>
<td>$\theta_{\text{As}}$</td>
<td>$2.0$ Å$^3$</td>
</tr>
<tr>
<td>$W_{\text{Ga-Ga}}$</td>
<td>$0.0$ J Å$^6$</td>
</tr>
<tr>
<td>$W_{\text{As-As}}$</td>
<td>$58.916 \times 10^{-18}$ J Å$^6$</td>
</tr>
<tr>
<td>$W_{\text{Ga-As}}$</td>
<td>$0.0$ J Å$^6$</td>
</tr>
<tr>
<td>$r_1$</td>
<td>$5.0$ Å</td>
</tr>
<tr>
<td>$r_4$</td>
<td>$3.75$ Å</td>
</tr>
<tr>
<td>$\theta_{ijk}$</td>
<td>$7.9 \times 10^{-19}$ J</td>
</tr>
<tr>
<td>$\theta$</td>
<td>$1.0$ Å</td>
</tr>
<tr>
<td>$r_0$</td>
<td>$3.8$ Å</td>
</tr>
<tr>
<td>$\theta_{ijk}$</td>
<td>$109.47^\circ$</td>
</tr>
</tbody>
</table>

3.4 Measurement of physical properties

To analyze and compare data from molecular dynamics simulations with other theoretical and experimental results, it is useful to generate data in a well-known and understandable format. Molecular dynamics generates, in principle, the time evolution of a system of particles, which is in and of itself of limited utility. By averaging over the instantaneous states of the system and using the equivalence of the time average and the
ensemble average in statistical mechanics, we can calculate other important physical properties of the system.

This approach has limitations. The assumption of equivalence between time and ensemble averaging can only be made if a phase space trajectory will pass through all state points in the configuration space, i.e. is space-filling. The property is referred to as ergodicity, and is affected by the equations of motion of the system and the length of the phase-space trajectory.

### 3.4.1 Thermodynamic quantities

The total energy of the system, given as the sum of kinetic and potential energy, $E = K + V$, where the kinetic energy is defined as

$$ K = \frac{1}{2} m_i \dot{r}_i^2 $$

(3.15)

and the potential energy is defined by Equation 3.8 for a general MD system. From this microscopic energy, we can calculate the temperature of the system by averaging over the entire ensemble:

$$ \langle K \rangle = \left\{ \frac{1}{2} m_i \dot{r}_i^2 \right\} = \frac{2}{3} N k_B T $$

(3.16)

or, stated simply, the average over all particles of the kinetic energy is proportional to the temperature of the system. In the proportionality constants, $N$ is the number of atoms in the system, and $k_B$ is the Boltzmann constant.

The pressure of the system is typically calculated by the virial theorem [39], given as

$$ P_{ij} = \frac{N k_B T}{V} \mathbf{I} + \frac{1}{2} \sum_{\substack{i,j \neq i}} \left( \frac{\mathbf{r}_{ij} \cdot \mathbf{F}_{ij}}{V} \right) $$

(3.17)
where $P_{ij}$ is the pressure tensor, $I$ is the identity matrix, $r_{ij}$ is the vector between atoms i and j, and $F_{ij}$ is the force on atom i due to atom j. Alternatively, the pressure can be calculated from the trace of the stress tensor, i.e.

$$P = \frac{1}{3} \text{Tr} \Sigma$$  \hspace{1cm} (3.18)

assuming that the stress is uniformly hydrostatic in nature. A form for the internal stress tensor is given in Equation 3.33.

Physical quantities can also be calculated from RMS fluctuations in thermodynamic variables. The constant-volume heat capacity is one such quantity, given by

$$\langle \Delta V^2 \rangle = \langle \Delta K^2 \rangle = \frac{3}{2} \frac{Nk_B T^2}{C_V}$$  \hspace{1cm} (3.19)

for the microcanonical ensemble. $\Delta V$ and $\Delta K$ are the changes in potential and kinetic energies respectively. In a similar fashion, the elastic constants of the solid can be calculated from a system in a isenthalpic-isostress ensemble [40, 41].

### 3.4.2 Structural correlations

Certain types of information about the structure of the system can be obtained from the pair correlation function $g(r)$. The pair correlation function is defined in terms of its partial components: the correlations between atoms of species $\square$ and species $\square$, where $\square$ and $\square$ are not necessarily distinct. The function is defined as

$$g_{\square\square}(r_1, r_2) = \frac{V^2}{N_{\square}N_{\square}} \left\langle \left[ \frac{\partial}{\partial \square_i} \right] \left[ \frac{\partial}{\partial \square_j} \right] \delta(r_1 - r_i) \delta(r_2 - r_j) \right\rangle, \hspace{1cm} (3.20)$$

where $N_{\square\square}$ are the number of atoms of each species and the angle brackets denote the ensemble average.
This expression can be simplified considerably if the system is translationally invariant. In such cases, pair correlation depends only upon the separation vector 
\[ r = r_1 - r_2 \] 
and can be written as
\[
    g_{ab}(r) = \frac{V}{N_aN_b} \left\langle \sum_{i \neq j}^{N_a} \sum_{j \neq i}^{N_b} \delta(r - r_{ij}) \right\rangle. 
\] (3.21)

Further simplification can be made if the system is isotropic as well. In this case, the expression can be averaged over all directions as well, yielding an expression dependent only upon \( r \), the scalar separation:
\[
    g_{ab}(r) = \frac{V}{4\pi r^2 N_a N_b} \left\langle \sum_{i \neq j}^{N_a} \sum_{j \neq i}^{N_b} \delta(r - r_{ij}) \right\rangle. 
\] (3.22)

In discrete systems such as MD simulations, it is convenient to formulate the pair correlation function in terms of sums over bins of finite width. To obtain the total pair correlation function, a weighted sum of the partial contributions is computed:
\[
    g(r) = \sum_{a,b} c_a c_b g_{ab}(r), 
\] (3.23)

where \( c_{a,b} \) are the concentrations of the species, given by \( N_{a,b} / N \). The coordination number for species \( \square \) can be obtained by integrating over the expression for partial pair correlation, giving the expression
\[
    N_{ab}(r) = \frac{4\pi N_a}{V} \int r^2 g_{ab}(r) dr. 
\] (3.24)

For comparison with experiment, the pair correlation function can be derived from the static structure factor, which are obtained from neutron scattering experiments. The structure factor is given by
\[
S_{\langle\langle}(\mathbf{q}) = \mathcal{D}_{\langle\langle} + \sqrt{c_{\langle\langle}c_{\langle\langle} \frac{N}{V} \int \mathbf{f}_{\langle\langle}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d^3 \mathbf{r}
\]

(3.25)

The integral term is clearly the Fourier transform of the partial pair correlation function. The structure factor measured by neutron scattering is related to Equation 3.25 by the following relation \[42\]

\[
S_{\langle\langle}(\mathbf{q}) = \mathcal{D}_{\langle\langle} + \sqrt{c_{\langle\langle}c_{\langle\langle} \int \mathbf{f}_{\langle\langle}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d^3 \mathbf{r}
\]

(3.26)

where the \( b_{\langle\langle} \) are the coherent neutron scattering lengths of species \( \square \) and \( \square \).

For GaAs, structure data from x-ray scattering is also used in validating the interatomic potentials used \[38\]. This data can be compared with the pair correlation function as well. The appropriate replacement for Equation 3.26 is given by

\[
S_{\langle\langle}(\mathbf{q}) = \frac{\mathcal{D}_{\langle\langle} \mathcal{D}_{\langle\langle} c_{\langle\langle} S_{\langle\langle}(\mathbf{q}) \sqrt{c_{\langle\langle}c_{\langle\langle}}}{\mathcal{D}_{\langle\langle} \mathcal{D}_{\langle\langle} c_{\langle\langle}}
\]

(3.27)

where the \( f_{\langle\langle} \) and \( f_{\langle\langle} \) are the x-ray form factors of species \( \square \) and \( \square \) respectively.

Pair correlation is typically insufficient for complete characterization of structure. Three-body correlations, measured by bond angle distributions, are also necessary to characterize solids. Bond angles are calculated by looping over triplets of “bonded” particles, which are defined on the basis of a cutoff length. Some bond angle distributions can be obtained experimentally from nuclear magnetic resonance (NMR) experiments.

Higher order correlations are not commonly used in characterization. One notable exception to this is the torsion angle, a four-body correlation. The torsion angle is useful
for determining the presence of stacking faults in certain crystals. More commonly, large-scale correlations such as fracture morphology and porosity are studied.

3.4.3 Dynamic correlations

In general, correlations between two quantities $A$ and $B$ can be measured by the correlation coefficient,

$$c_{AB} = \frac{\langle A \Box (A) \rangle \langle B \Box (B) \rangle}{\sqrt{\langle A^2 \rangle \langle B^2 \rangle}},$$  \hspace{1cm} (3.28)$$

where $\langle [A^2] \rangle = \langle A^2 \rangle \Box [A^2]$, which is the fluctuation of quantity $A$. When both $A$ and $B$ are functions of time, the correlation is dynamic, and we can extend Equation 2.32 in the following fashion

$$c_{AB}(t) = \frac{\langle A(t_A) \Box (A(t_A)) \rangle \langle B(t_B) \Box (B(t_B)) \rangle}{\sqrt{\langle A(t_A)^2 \rangle \langle B(t_B)^2 \rangle}},$$  \hspace{1cm} (3.29)$$

where $t = |t_A - t_B|$. If quantities $A$ and $B$ are the same, the resulting $c_{AA}(t)$ is called an autocorrelation function and measures the correlation of a quantity at some time with the same quantity at another time. The absolute value of the normalized correlation function varies between 0 and 1 with higher degrees of correlation represented by larger values. Correlation functions can be used to measure transport coefficients, such as the diffusion constant and thermal conductivity.

The diffusion constant is measured by calculating the velocity autocorrelation function,

$$Z(t) = \frac{\langle v_i(0) \cdot v_i(t) \rangle}{\langle v_i^2(0) \rangle},$$  \hspace{1cm} (3.30)$$
for some species, \( \mathcal{Q} \). The velocity autocorrelation function is related to the self-diffusion constant \( D_\mathcal{Q} \) by

\[
D_\mathcal{Q} = \frac{k_B T}{m_\mathcal{Q}} \frac{1}{\mathcal{Q}} \int Z_\mathcal{Q}(t) dt \tag{3.31}
\]

The diffusion constant can also be calculated from the mean-square displacements of atoms by

\[
D_\mathcal{Q} = \lim_{t \to \infty} \frac{\langle \mathbf{r}(t) \cdot \mathbf{r}(0) \rangle}{6t} \tag{3.32}
\]

By taking the Fourier transform of the velocity autocorrelation function, a function proportional to the phonon density of states can be obtained. This is useful for comparison with experimental results and is used to validate interatomic potentials.

### 3.4.4 Mechanical properties

Stress, like pressure, requires application of the virial theorem in its computation. A general expression for stress is

\[
\sigma_{\mathcal{AB}} = \frac{1}{V} \left\{ \sum_i \left[ m_i v_i^\mathcal{A} v_i^\mathcal{B} + r_i^\mathcal{A} f_i^\mathcal{B} \right] \right\}, \tag{3.33}
\]

where the \( \mathcal{A}, \mathcal{B} \) are Cartesian indices, and the index \( i \) represents individual atoms. Care must be taken using Equation 3.33 in systems with periodic boundaries, since the expression does not take the minimum image convention into account. If the forces, \( f_{ij} \), are short-ranged only, then the separations, \( r_{ij} \), are the minimum image separations, otherwise this problem can be handled by redefining Equation 3.33 to be independent of the system origin or by summing over both real and image particles.

Local stress distributions are most often of interest in molecular dynamics problems. Calculating local stresses for extremely small volumes can be problematic,
however, because stress is related to an assumption of continuity and is thus not well defined on this scale. Two approaches are typically used to account for this: the mechanical approach and the virial definition. The virial definition is the most straightforward, as it simply restricts the summation in Equation 3.33 to atoms in a specific volume [43]. This can be extrapolated to a definition of atomic stress, which is the contribution of a single atom to the sum. The direct mechanical approach takes the stresses to be acting on surface elements. By dividing the MD system into small subcells, the local stresses inside the subcells can be computed in terms of the stresses acting on the faces of the cell. While it has been argued [44] that this is a more appropriate choice for a definition of stress, the virial approach typically yields smoother behavior.

Once we have a reasonable definition of stress, several more mechanical properties become available to us. One of the more important of these quantities is the Young’s modulus, which is the typical quantity used to measure a material’s resistance to elastic deformation. The Young’s modulus, $E$, is defined by

$$E = \frac{\sigma}{\epsilon},$$

(3.34)

where $\sigma$ is uniaxial stress, and $\epsilon$ is uniaxial strain. This relation is only valid in the elastic regime; the onset of plastic deformation is indicated by a breakdown in the relation. The point at which this breakdown occurs is termed the yield point.

The Young’s modulus can be calculated with molecular dynamics simulations in a straightforward fashion by applying a small strain along one axis of an MD system and measuring the resultant stress. Experimentally, Young’s modulus is measured by obtaining the stress-strain curve, typically by some sort of tension test, and finding the
slope of the stress-strain curve in the elastic regime. Young’s modulus can also be calculated from indentation experiments as described in Section 2.2.
CHAPTER 4

NUMERICAL AND COMPUTATIONAL TECHNIQUES

4.1 Properties of integration algorithms

Solving differential equations in an iterative fashion both quickly and accurately is essential to MD simulations. For accuracy and stability, we are interested in integrators that solve the Hamiltonian problem while meeting certain conditions for stability over long ranges of time and accuracy for short ranges of time.

Long-term stability is characteristic of symplectic integrators. These integrators are based upon canonical transformations of phase space and thus require that all canonical invariants remain conserved. The short-term accuracy of the solution is most significantly affected by the size of the time step used in the integrator. This is an unsurprising fact, as it is easily inferred from the similar effects of reducing the step size in a Simpson’s or trapezoid rule integration of a function. The reduction of time step, however, limits the length of the simulation. Since each time step requires a calculation of forces, the most compute-intensive step of the integration, it is clear that the length of the simulation is constrained by the number of steps in the simulation. For this reason, long step sizes are desirable.

The key property of symplectic integrators is the conservation of phase space volume. We can write this condition quantitatively in terms of a Jacobian [45],
\[
\frac{\partial (p, q)}{\partial (p, q)} = \begin{bmatrix}
\frac{\partial p}{\partial p} & \frac{\partial p}{\partial q} \\
\frac{\partial q}{\partial p} & \frac{\partial q}{\partial q}
\end{bmatrix}
\] (4.1)

An integrator is termed symplectic only if the determinant of this Jacobian is equal to one.

Symplecticness is related to the concept of energy conservation. For the microcanonical ensemble, the total system energy is the conserved quantity of the exact solution to the Hamilton equations; other ensembles have different conserved quantities, related to the total energy plus the fictitious energies of the thermostats, barostats and other controls attached to the system. Since the numerical solutions are approximations, the errors in the integration show up as non-conservation of energy.

In can be proven [46] that symplectic integrators cannot exactly conserve energy. They do, however, conserve energy very well within approximation and the errors due to the approximation are exponentially small and are also bounded [45]. It is this property that makes them well suited for use in molecular dynamics simulations.

4.2 The Gear predictor-corrector algorithm

One of the earlier integrators used in MD simulations is the classic Gear predictor-corrector algorithm [47]. The Gear algorithm begins by estimating the positions, velocities, accelerations, and further time derivatives at time \( t + \Delta t \) by a Taylor expansion around \( t \). Typically, for the MD problem, two further time derivatives are used, although one or three further derivatives are not uncommon choices. The Taylor expansion yields the following equations:
\[ \mathbf{r}_p(t + \Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}(t) \Delta t + \frac{1}{2} \ddot{\mathbf{r}}(t) \Delta t^2 + \frac{1}{6} \mathbf{r}^2(t) \Delta t^3 + \cdots \]
\[ \mathbf{v}_p(t + \Delta t) = \mathbf{v}(t) + \dot{\mathbf{v}}(t) \Delta t + \frac{1}{2} \ddot{\mathbf{v}}(t) \Delta t^2 + \frac{1}{6} \mathbf{v}^2(t) \Delta t^3 + \cdots \]
\[ \mathbf{a}_p(t + \Delta t) = \mathbf{a}(t) + \dot{\mathbf{a}}(t) \Delta t + \frac{1}{2} \ddot{\mathbf{a}}(t) \Delta t^2 + \frac{1}{6} \mathbf{a}^2(t) \Delta t^3 + \cdots \]
\[ \mathbf{b}_p(t + \Delta t) = \mathbf{b}(t) + \cdots \] (4.2)

where \( \mathbf{b} \) denotes the time derivative of acceleration, and the \( p \) subscript indicates that these are predicted values. Note that if further time derivatives of acceleration were used, then more equations would be added to the system.

At this point the forces, and thus the accelerations are computed from the values of the predicted positions, and the errors computed by

\[ \Delta \mathbf{a}(t + \Delta t) = \mathbf{a}_c(t + \Delta t) - \mathbf{a}_p(t + \Delta t), \] (4.3)

where the \( \mathbf{a}_c \) are the computed, or corrected, accelerations. The other values in the integrator are adjusted based on this error, by

\[ \mathbf{r}_c(t + \Delta t) = \mathbf{r}_p(t + \Delta t) + c_0 \Delta \mathbf{a}(t + \Delta t) \]
\[ \mathbf{v}_c(t + \Delta t) = \mathbf{v}_p(t + \Delta t) + c_1 \Delta \mathbf{a}(t + \Delta t) \]
\[ \mathbf{a}_c(t + \Delta t) = \mathbf{a}_p(t + \Delta t) + c_2 \Delta \mathbf{a}(t + \Delta t) \]
\[ \mathbf{b}_c(t + \Delta t) = \mathbf{b}_p(t + \Delta t) + c_3 \Delta \mathbf{a}(t + \Delta t) \] (4.4)

where the \( c_i \) are constant coefficients. Gear tabulated [47] appropriate values for these coefficients, based on the order of the differential equation being solved and the number of time derivatives calculated and used.

The Gear algorithm, while still popular, has significant drawbacks. The most egregious of these is the memory requirement. Assuming a five quantity integrator, i.e. using up to the fourth time derivative of position, the integrator requires 15 words of storage for each particle. In the common case of 8 byte double precision floating-point numbers, this is equivalent to 120 bytes per atom. As the number of particles scale into the tens and hundreds of millions, this becomes a real limitation. Further, since the Gear
integrator is not known to be symplectic, the algorithm typically requires smaller steps of \( \Delta t \) than other methods in order to maintain acceptable accuracy.

### 4.3 Verlet integrators

The Verlet integrators are another class of integrators. One of these, the velocity-Verlet integrator, is particularly well suited to the MD problem. The Verlet integrator is also derived from a Taylor series expansion. Taking two expansions around \( r(t) \),

\[
\begin{align*}
\mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \Delta t \mathbf{v}(t) + \frac{1}{2} \Delta t^2 \mathbf{a}(t) + O(\Delta t^3) \\
\mathbf{r}(t) &= \mathbf{r}(t) + \Delta t \mathbf{v}(t) + \frac{1}{2} \Delta t^2 \mathbf{a}(t) + O(\Delta t^3)
\end{align*}
\]  

and adding them together, we have

\[
\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t) - \Delta t \mathbf{v}(t) + \Delta t^2 \mathbf{a}(t) + O(\Delta t^3). \tag{4.6}
\]

We can apply Equation 4.6 to evolve our system, by using the positions at the current and prior time along with the forces to generate the positions at the next timestep. While the compactness of this algorithm is quite attractive, the requirement of two initial positions is a limitation.

This requirement of the Verlet integrator can be alleviated by using the velocity-Verlet integrator. We write this integrator as

\[
\begin{align*}
\mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \Delta t \mathbf{v}(t) + \frac{1}{2} \Delta t^2 \mathbf{a}(t), \\
\mathbf{v}(t + \frac{1}{2} \Delta t) &= \mathbf{v}(t) + \frac{1}{2} \Delta t \mathbf{a}(t), \\
\mathbf{v}(t + \Delta t) &= \mathbf{v}(t + \frac{1}{2} \Delta t) + \frac{1}{2} \Delta t \mathbf{a}(t + \Delta t),
\end{align*}
\]  

where the \( \mathbf{a}(t + \Delta t) \) are the accelerations due to the forces on the particles after the position update in the first equation [48]. The velocity-Verlet integrator resembles a three-value predictor-corrector integrator. It has the same advantage in compactness as the simple Verlet integrator, requiring only nine words of storage per particle, but improves upon the
initial condition requirements by replacing the requirement of initial positions at two
different times with an initial position and an initial velocity at the same point in time.
Additionally, the velocity-Verlet integrator is relatively simple to implement in code and,
importantly, it is symplectic [49, 50].

4.4 Reference system propagator algorithms

Tuckerman et al. [50] recently derived a class of integrators known as reference
system propagator algorithms (RESPA) that, in addition to their general stability, can
take advantage of multiple length and time scales in simulation to preserve accuracy even
at relatively large time steps.

Following the derivation of Tuckerman [50], we write the Liouville operator in
Cartesian coordinates as

\[
\begin{align*}
\dot{L} &= \sum_{j=1}^{N} \frac{\partial}{\partial \mathbf{x}_j} \mathbf{p}_j + \frac{\partial}{\partial \mathbf{p}_j} \mathbf{F}_j. \\
\end{align*}
\]

(4.8)

We can then write the state of the system \( \mathbf{G} \) at some time, \( t \), as

\[
\mathbf{G}(t) = U(t) \mathbf{G}(0),
\]

(4.9)

where

\[
U(t) = e^{iL t}
\]

(4.10)

is the classical propagator. The propagator is time reversible in the sense that \( U(t) \) is a
unitary operator:

\[
U(\mathbf{G}) = U^{-1}(t).
\]

(4.11)

If we break the Liouville operator into two parts, such that

\[
iL = iL_1 + iL_2,
\]

(4.12)
then we can apply the Trotter expansion for small time intervals to $U(t)$. This results in the following:

$$U(t) = e^{i(L_1 + L_2)t}$$

$$= e^{i\mathcal{H}_1 t} e^{i\mathcal{H}_2 t} + O(t^3)$$

$$= U_1(t) U_2(t) U_1(t) + O(t^3). \quad (4.13)$$

We are free to choose the decomposition of the Liouvillian in a convenient fashion. The most obvious such decomposition,

$$iL_1 = \sum_{j=1}^{N} \frac{\partial}{\partial r_j}$$

$$iL_2 = \sum_{j=1}^{N} \frac{\partial}{\partial p_j}, \quad (4.14)$$

when substituted into Equation 4.13 gives

$$U(t) = \exp \left( \frac{t}{2} \sum_{j=1}^{N} \frac{\partial}{\partial r_j} \right) \exp \left( \sum_{j=1}^{N} \frac{\partial}{\partial p_j} \right) \exp \left( \frac{t}{2} \sum_{j=1}^{N} \frac{\partial}{\partial r_j} \right). \quad (4.15)$$

Applying Equation 4.15 to a system state $\{\{\rho(t), \psi(t)\}\}$, and applying the following property:

$$e^{a \partial_x} f(x) = f(x + a), \quad (4.16)$$

we can recover the velocity-Verlet integrator:

$$\dot{\mathbf{r}}_i(t + \frac{\Delta t}{2}) = \dot{\mathbf{r}}_i(t) + \frac{\Delta t}{2m_i} \mathbf{F}_i(t),$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \dot{\mathbf{r}}_i(t + \frac{\Delta t}{2}),$$

$$\ddot{\mathbf{r}}_i(t + \Delta t) = \ddot{\mathbf{r}}_i(t + \frac{\Delta t}{2}) + \frac{\Delta t}{2m_i} \mathbf{F}_i(t + \frac{\Delta t}{2}). \quad (4.17)$$
Simple inspection reveals that Equations 4.17 and 4.7 are identical. This derivation of
the velocity-Verlet scheme from a unitary operator implies that the scheme is time-
reversible as well.

It is of great utility to be able to treat different parts of the MD system with
different time steps. This is especially the case in systems where the forces are primarily
short-ranged. In such systems, the contribution to the force from far atoms changes less
rapidly than the contributions of near atoms. One can decompose the Liouvillian to take
advantage of this. By making the decomposition

$$iL = iL_s + iL_l, \quad (4.18)$$

where

\[ iL_s = \sum_j \left( f_j' \frac{\partial}{\partial r_j} + f_j \frac{\partial}{\partial p_j} \right) \]

\[ iL_l = \sum_j \frac{\partial}{\partial p_j} \]

(4.19)

we can use the Trotter factorization to obtain

$$U_{sl}(\Delta t) = \exp \left[ \frac{\Delta t}{2} \sum_j f_j' \frac{\partial}{\partial p_j} \right] \exp \left[ (iL_s)\Delta t \right] \exp \left[ \frac{\Delta t}{2} \sum_j f_j' \frac{\partial}{\partial p_j} \right]. \quad (4.20)$$

We can then take the time step $\Delta t$, and divide it into n parts,

$$U_{sl}(\Delta t) = \exp \left[ \sum_j f_j' \frac{\partial}{\partial p_j} \exp \left( iL_s \frac{\Delta t}{n} \right) \right]^n \exp \left[ \sum_j f_j' \frac{\partial}{\partial p_j} \right]. \quad (4.21)$$

By applying the decomposition (4.14) to the central term of (4.21) and using the Trotter
factorization again, we can write

$$\exp(iL_s) = \left[ \exp(iL_s \frac{\Delta t}{n}) \right]^n$$
\[ \begin{align*} 
&= \exp \left[ \sum_{n} \int \sum_{j} f_j \frac{\partial}{\partial p_j} \right] \exp \left[ \sum_{n} \int \sum_{j} \dot{r}_j \frac{\partial}{\partial r_j} \right] \exp \left[ \sum_{n} \int \sum_{j} f_j' \frac{\partial}{\partial p_j} \right] \end{align*} \] (4.22)

This decomposition allows the integrator to update the short-range forces and positions \( n \) times between each long-range update. This scheme gives considerable time savings when applied to the appropriate systems.

While the prior examples generate propagators for systems in the microcanonical ensemble, it is also possible to generate such propagators for other thermodynamic ensembles. RESPA algorithms have been derived for the canonical ensemble and NPT ensembles [28, 32, 49]. Full derivations and suggestions for the implementation of the propagators in code can be found in Ref. [49].

### 4.5 Short vs. long-range forces

Separating short and long range forces in a simulation must be done in such a way as to maximize the efficiency of the multiple time step propagator while minimizing the associated error. Further, the separation must be done smoothly so that no artifacts are generated. The method most commonly used involves using a smooth function as a filter on the potential curve. One such function can be defined piecewise as

\[ S(r) = \begin{cases} 
1, & r < r_s \land w \\
1 + \frac{(r - r_s w)^2}{2(r - r_s w)w^2}, & r_s w < r < r_s \\
0, & r > r_s 
\end{cases} \] (4.23)

With a switching function thus defined, we can apply it to the two body potential function, or the forces derived from the potential, so that

\[ V^{(2)}(r) = S(r)V^{(2)}(r) + \left[ I \otimes S(r) \right] V^{(2)}(r). \] (4.24)

We can then define
\[ V_s^{(2)}(r) = S(r)V^{(2)}(r), \]
\[ V_l^{(2)}(r) = \left[ 1 - S(r) \right] V^{(2)}(r), \]  \hspace{1cm} (4.25)

where the \( s \) and \( l \) denote short and long range respectively. Not accounted for in Equations 4.23-24 is the cutoff distance beyond which no atoms contribute to the potential. Figure 4.1 illustrates the long vs. short range switching function. For the multiple time step formalism, \( V_s \) for the green atom in Figure 4.1 would be updated every time step, whereas \( V_l \) would be updated less frequently.

Figure 4.1: Switching function ranges. The lighter blue region is the first region in Eqn. 4.23, where the forces are exclusively short range. The darker blue is the transition region, and the unshaded area is the region defined as long range. A cutoff distance is typically implemented, but is not illustrated here.
This separation of short and long-range forces dovetails well with the most common data structure for storing particles in MD simulations. This method, referred to as the linked cell method [51], divides the simulation space into small cubic cells with dimensions slightly larger than the force cutoff. This is expressed as $r_c + d$, where $d$ is referred to as the “skin.” Each cell is represented by a linked-list of the atoms within it. By using this data structure, the order $N^2$ search for neighbors becomes an order $MN$ search. Since the cell dimension is based on the cutoff for interactions, only the lists of atoms in the central cell and neighboring cells must be traversed. The quantity $M$ is thus the total number of atoms in those lists. For large systems, it is clear that $M << N$. Figure 4.2 shows a schematic of the linked cell method.

![Figure 4.2: An MD system in two dimensions with the cell boundaries superimposed. The light blue overlay shows the area within the cutoff radius of the green atom.](image)

The number of lists to be traversed can be cut in half by computing a list of neighbors before calculating the forces. This neighbor list method, due to Verlet [52], is
simply a tabulation of the results of a search for neighbors. By taking advantage of symmetry, i.e. if atom A is a neighbor of atom B then the converse must also be true, only half the neighboring cells must be traversed to compute the neighbor list.

Additionally, the force computation is reduced to a traversal of the neighbor list for each atom. This makes the force computation exactly $<M>N$ steps, where $<M>$ is the average number of neighbors for each atom.

Figure 4.3: (a.) For any atom in the dark blue central cell, only the atoms in the adjacent light blue cells must be searched for neighbors. (b) By building a neighbor list first, only half the adjacent cells must be searched.

4.6 Implementation of molecular dynamics on parallel computers

The data structures and techniques described in the last section can be implemented quite efficiently on both serial computers as well as distributed memory parallel computers. Of the various parallel architectures available, distributed memory systems are currently receiving the most attention due to efforts such as the Beowulf Project at Los Alamos National Laboratory [53]. A typical distributed memory architecture is represented in Figure 4.4.
For such a computer to be efficient, it is clear that the total MD system must be divided up amongst the processors in some fashion. The most common choice of decomposition is spatial domain decomposition, where the system is divided up on the basis of the atomic positions. Each processor will thus have some subvolume of the MD system resident in its memory. Any atom that crosses the boundary will thus be transferred from one processor to another in a message-passing step, and forces due to atoms in adjacent domains must be transferred as well.

It is highly desirable for any algorithm being implemented on a distributed memory architecture of the type shown in Figure 4.4 to minimize the amount of communication between CPUs. It is obvious that a network message-passing step must

Figure 4.4: Schematic of a typical distributed memory parallel computer. Portions of the simulated system are mapped on to each CPU and the network allow passing of atoms that cross domain boundaries to the CPU responsible for that domain.
block computation until all communication is finished. Further, if an algorithm is poorly designed, it will require much more communication to complete than a more efficiently designed algorithm. The efficiency of a parallel algorithm is defined by the speedup

\[ S = \frac{t_{\text{serial}}}{t_{\text{parallel}}}, \]

which is essentially the time for the algorithm to complete on one processor divided by the time to complete on multiple processors. Dividing the speedup by the number of processors yields a percentage efficiency, where a value of 1 indicates perfect parallel efficiency. The ideal parallel algorithm has a reasonably high parallel efficiency for any number of processors. If the plot of efficiency vs. processor is roughly horizontal, the algorithm is termed scalable.

The neighbor list technique plays an important role in making the interprocessor communication step efficient. By storing an image of the linked cells adjacent to the domain boundary in neighboring cells (see Figure 4.5), we reduce the communication to one well-defined message-passing step at the cost of adding to the per-node storage requirement.

Since the linked-cell widths are based on the force cutoff distances, it is guaranteed that all atoms necessary for local force calculations are stored in local memory. This condition assumes that there is a force cutoff. Long-range forces, such as the full Coulomb force, will not meet this criterion. A further advantage, assuming the domain size is sufficiently large with respect to the particle velocities, is that all internode communication will be between neighboring nodes. This considerably decreases the amount of time necessary to complete the communication step.
Figure 4.5: Atoms adjacent to the domain boundary in neighboring domains are cached on the local processor. The small grid represents linked-cell boundaries, while the larger grid represents node boundaries. In this figure, the 16 linked cells shaded blue are cached on the node that they border.

One key issue when choosing the decomposition is load balance. If one or more processors have significantly more particles resident, these processors will slow down the performance of the entire system, thereby adversely affecting the parallel efficiency of the program. Dynamic load balancing algorithms exist and are reasonably effective (see, for example, Ref. [54]), but must typically be designed for specific applications. The simulations performed for this dissertation did not use any dynamic load balancing technique.

While calculating the actual dynamics of the system may not require all-to-all communications, such may be necessary to compute long-range structural correlations, such as pair-distribution. In these cases, the communication is efficiently accomplished by ordering the nodes in a ring topology [55], as shown in Figure 4.6. In this method,
a system of $P$ processors would require $\lceil P/2 \rceil$ message passing steps, where $\lceil \cdot \rceil$ denotes the integer ceiling.

In order to prevent a deadlock condition, the nodes are assigned an even-odd parity. Each message passing step, denoted by $s$, consists of two parts: (i) each even-parity node $p$ sends its data to the odd node $(p + s) \mod P$, while the odd nodes listen. (ii) each odd node $p$ sends its data to the even node $(p + s) \mod P$, while the even nodes listen. In this scheme, the target nodes are always assured of being ready to receive
messages and thus deadlock is prevented. Using this strategy, the time necessary to complete a full pair correlation scales as $N^2/P$.

4.7 Langevin dynamics

Langevin dynamics is a technique by which the NVT ensemble can be approximated. Essentially, Langevin dynamics adds a dissipative component to the interparticle force. At each time step, a small fraction of the kinetic energy of each atom is removed from the system and replaced by a fraction of a random velocity from a distribution about a target temperature. This takes the form of

$$v' = v - D_t \frac{\partial}{\partial t} v + D_t v_T,$$  \hspace{1cm} (4.26)

where $v'$ is the adjusted velocity, $v$ is the original velocity, $v_T$ is a random velocity from a distribution about temperature $T$, $D_t$ is the timestep of the system and $t$ is the Langevin characteristic time. This characteristic time is the key parameter of this scheme: it determines how quickly the system tends towards the target temperature $T$. As $t$ goes towards infinity, the effect of the Langevin scheme becomes insignificantly small, and as it goes to 1, it effectively destroys any time correlations in velocity. This is important to note if one is attempting to calculate such properties as the phonon density of states. The advantage of the Langevin technique, however, is that it effectively thermostats each atom individually, thus allowing effective equalization of highly localized regions of temperature.
CHAPTER 5

NANOINDENTATION SIMULATIONS ON GaAs FILMS

5.1 Treatment of the indenter

For indentation experiments, it is crucial that the indenter be essentially rigid with respect to the substrate material. For this reason, silicon nitride is the material of choice for experimental nanoindenters while diamond serves the same purpose in experimental microindenter apparati. For the indentation simulations reported here, rather than to model a complete indenter-substrate interaction, an idealized indenter potential was used while simultaneously holding the atoms of the indenter rigid.

This idealized indenter potential consists solely of the short-ranged (~ r\(^{-11}\)) steric repulsion term from Equation 3.12. The steric parameter, \( \vartheta \) from Equation 3.12, of the indenter atoms was made large with respect to the indenter lattice constant, thereby causing an effective overlap between indenter atoms. This prevented substrate atoms from diffusing into the indenter.

The indenter atoms were not allowed to contribute to energy of the system; similarly, they were ignored for calculation of stress, coordination number, pair correlation, and other quantities. Due to the indenter’s rigidity, the indenter was moved in discrete steps per some fixed number of timesteps. To avoid unphysical effects due to this discretization, the length of these steps was chosen to be small with respect to the force cutoff length for the interatomic potential.
The modelled indenter had a diamond structure, with a lattice constant consistent with that of silicon. Increasing the constant associated with the steric repulsion for the fictitious indenter atoms compensated for the increased lattice spacing for the purpose of preventing diffusion into the indenter. This lattice constant was chosen to reduce the total number of atoms in the indenter. By doing so, the percentage of atoms in the system that were in the indenter was kept to a minimum, thus increasing the efficiency of the simulation.

Indenter updates took place at the end of the molecular dynamics loop. Every time a molecular dynamics loop was completed, a check was done to see if it was time for an indenter update. These indenter updates typically took place every 5 timesteps, with a timestep of 2.2 fs. Figure 5.1, below, illustrates the indenter logic.

For this simulation, the shape of the indenter was chosen to be a modified Vickers type indenter. It thus had the geometry of a square-based pyramid, however, instead of the typical Vickers tip angle of 148.1°, a tip angle of 90° was used. The calculations from elasticity theory describing the behavior of indenters on an elastic half-space indicate that so long as the indenter is a solid of revolution of a smooth function, such as a paraboloid, the elastic behavior of the substrate is geometry independent [13].

Furthermore, the results from elasticity theory for nonsmooth indenters are found to only differ from the results from the smooth indenters by a small geometry-dependent constant [56]. This deviation does not exceed 1.2% for a square-based flat punch. These results indicate that variations in the tip angle will not significantly affect the results of the simulation. Also, it is considered desirable to have a sharply pointed tip for shallow indentations [9].
Figure 5.1: Flowchart illustrating the indenter update logic. This decision loop is not entered every timestep; rather, a parameter controlling the number of timesteps between each indenter update is passed to the program at the beginning of the simulation. At the end of this loop, the average x, y, and z components of the force are stored along with the center of mass of the indenter for this timestep, and the positions of the indenter atoms are updated.

Because of the desirability of tip sharpness, many thin film indentations are done with the triangular-based Berkovich indenter [57]. This is because the specifications of the Vickers indenter allows for slight imperfections in the tip as illustrated in Figure 5.2, below. The Berkovich indenter specification for tip radius is less than 0.1 µm.
Since it is relatively simple to generate “perfect” Vickers indenters for simulation, where the offset as defined in Figure 5.2 is zero, this was done for the simulations reported here. This geometry was particularly desirable, since the alignment of the indenter diagonals along low-index directions is of interest considering the results of prior indentation simulations on silicon nitride performed by Walsh [24], where subsurface microcracking was observed in low-index directions along the indenter diagonals. With a perfect indenter, the diagonals are straight lines, rather than being broken by the offset, and thus this alignment is possible. Further, the Vickers geometry can be aligned with low index directions in a cubic crystal due to its square base.

Figure 5.2: Vickers indenter geometry. The offset is exaggerated for clarity. For microindentation, the specifications for the Vickers indenter have the offset width no more than 0.5 µm.

In the simulations reported in this dissertation, the load on the indenter was calculated by summing the reaction forces from the substrate atoms on the indenter atoms. The z-component of this force is the applied load, as it represents the force necessary to maintain the indenter’s position. The convention used for reporting
displacement was to define the depth of the indenter as the difference between the average position of the surface layer of the substrate before indentation and the minimum position along the z-axis of any atom in the indenter. Negative depths represent the separation between the tip and the surface. As illustrated in Figure 5.1, the indenter control code returns the centroid of the indenter. Before the simulations were started the difference between the z position of the centroid and the tip was measured. This offset did not change during the simulation since the atoms were held rigid. The indenter position data were then adjusted by this offset in a spreadsheet after the completion of the simulations. All indenter motion was in the positive or negative z direction only; no lateral motion was allowed.

**5.2 Substrate construction and geometry**

For the simulations of nanoindentation reported in this chapter, a slab-shaped system was constructed. The system had dimensions of 399.6 Å x 401.4 Å x 139.9 Å. This represents 100 unit cells by 71 unit cells by 35 unit cells, using a tetragonal unit cell of dimensions 3.997 Å x 5.653 Å x 3.997 Å that contains 4 atoms. The conventional cubic unit cell of GaAs is 5.653 Å in each direction at 300 K, and contains 8 atoms. The close-packing directions in the GaAs unit cell are <111>, and the nearest neighbor distance is 2.45 Å.

Periodic boundary conditions were applied along the system’s x and y directions, corresponding to the GaAs $[\bar{1}10]$ and [001] crystallographic directions respectively. In the system’s z direction, corresponding to the GaAs [110] crystallographic direction, the periodic condition was not applied, resulting in a free (110) surface. This particular choice of surface of GaAs is convenient as it is electrically neutral and thus does not
undergo the extensive surface reconstruction that is typically observed in the \{100\} family of planes. The resulting slab contained approximately one million atoms. Figure 5.3 shows the schematic of this system.

![Figure 5.3: Schematic diagram of the GaAs system.](image)

In order to simulate this system on a parallel computer, a spatial domain decomposition was applied as discussed in Section 4.6. The choice of decomposition for this system was an array of rectangular prisms whose \(z\) dimension was equal to that of the simulation cell. The system was decomposed onto 32 processors, with 8 subdivisions in the \(x\) direction and 4 subdivisions in the \(y\) direction. The simulations reported in Chapter
5 were performed on the CCLMS Linux cluster and the IBM SP3 at the Naval Oceanographic Office Major Shared Resource Center.

The slab was created by first generating a bulk lattice, periodic in all directions, with the desired dimensions. The simulation cell was then expanded in the z-direction, leaving two free surfaces. The energy from adding these free surfaces was then dissipated at $T = 0$ K for 2000 timesteps using Langevin dynamics with the characteristic time parameter $\tau$, as given in Equation 4.26, set equal to 100 $\tau t$. The system was then heated slowly to 300 K over 2000 timesteps using the same characteristic time parameter. This schedule is illustrated in the vertical steps in Figure 5.4.

The indenter was then inserted into the slab and withdrawn according to the schedule diagrammed in the horizontal steps in Figure 5.4. The Langevin characteristic time parameter, $\tau$, was set to 1000 $\tau t$ during the loading and unloading cycle. In order to allow the transient forces and vibrations to decay, the loading schedule was separated into a loading phase, where the indenter was either lowered or raised 1 Å over 500 $\tau t$, which is equivalent to a traversal rate of 100 m/s, and a holding phase, where the indenter was held in place for 1500 $\tau t$. At this point, all system data were written to disk and the process was repeated until the total traversal was completed. During the loading cycle, the bottom 4 Å of the slab were held rigid to prevent the substrate from moving.

The decay of the applied load during the holding phase was fitted to determine if anything could be said about the nature of the decay in the force on the indenter. A decay constant determined from curve fitting could be compared with other materials and used to quantitatively determine an optimum length of the holding period. For this fit, the system was held for 50 ps, or approximately 23000 timesteps, and the load was recorded.
every 10 timesteps. Neither exponential nor power law fitting yielded satisfactory results for the fitting the decay data. Using a high-order \((x^9)\) polynomial yielded slightly better results, but the \(R^2\) value for the fit was still less than 0.95, indicating a poor fit. Given this, nothing quantitative could be determined about the decay constant. Therefore, the holding phase length was made to be as long as possible within the limitation of the total amount of computer time available to perform the simulation.

![Indenter schedule](image)

Figure 5.4: Indenter schedule. Note that the flowchart only depicts the loading half of the full traversal. Unloading was done by the same schedule depicted by the blue elements, from maximum load until the indenter reached its original position before the traversal.

5.3 Load-displacement curves and mechanical properties

The load computed at the end of each cycle is an average of the load on the indenter during the last 100 steps of the hold phase. This gives a more accurate depiction of the load during the simulation, since transient forces due to the indentation process are allowed to decay. This decay was not smooth; the value of the load fluctuated during the
decay. By choosing 100 steps to average, the effect of the fluctuations was smoothed out to yield a reliable value for the load. The effect of this averaging can be seen by comparing the load-displacement curves from a traversal where the indenter was loaded continuously (Figure 5.5) to the load-displacement curve from a simulation where the holding phase is present (Figure 5.6).

Hardness was computed from the load-displacement curve in Figure 5.6 and the residual damage. The peak load was defined by the data point representing the average value of the load during the end of the holding phase at the end of the loading half of the traversal. The residual damage was found by measuring the width the pockmark at the indenter diagonal. At the atomic level, it is difficult to say precisely what the length of the diagonal would be. We chose a definition that was easy to replicate thus allowing accuracy and repeatability of the measurement.

Figure 5.5: Load-displacement curve with continuous loading.
Figure 5.6: Load-displacement curve with holding phase. Compare the peak load to Figure 5.5. Also note that the curve overall is smoother. The smoothness is due to the averaging done at the end of each holding phase.

The technique we used selected the atoms in the surface layer that lay within 1Å of the line of the indenter diagonal as defined by the centroid of the indenter. The maximum distance between the atoms on either side of the damage region was considered to be the length of the diagonal of the damage pockmark. Figure 5.7 illustrates the geometry of the pockmark cross-section.

This technique was implemented using a small Perl program. To determine the optimal parameter, a series of different slice widths, 2 Å, 3 Å, and 4 Å, were used. These different width filters were then moved from a position centered on the indenter diagonal by one quarter and one half the filter width in each direction. From the table generated by these different widths and positions, the maximum indenter diagonal was read. The 2 Å width was considered optimal because the total variation in the computed diagonal
Figure 5.7: Schematic of determination of the length of the diagonal of the residual damage. The atoms shown are all atoms in the top few layers that fall within 1 Å in each direction from the indenter diagonal.

length varied the least for that width. The maximum diagonal distance was determined to be appropriate by the simple argument that any shorter distance would not represent the true diagonal, but rather a line offset from the indenter diagonal by a small amount. In every case, a 2 Å width about the centroid line seemed to provide the best results.

From this data, we calculated that the hardness of the GaAs (110) surface was approximately 11.7 GPa. To the best of our knowledge, experimental data for nanoindentation of GaAs does not exist in the literature. Microhardness values for GaAs, however, do exist. For the (110) plane, the Knoop microhardness has been found to be 7.35 GPa [58]. Although the Knoop and Vickers hardness scales are different, they only differ by at most 10% for homogeneous samples [57], making a direct comparison reasonable.

This measurement does not take into account the negative photoplastic effect that GaAs exhibits [59]. Under illumination in the infrared range, GaAs softens more than
20%, as measured by Vickers indentation on the (100) surface. To the best of our knowledge, data characterizing the photoplastic effect on the (110) surface does not exist, nor are the details of the experiments quoted in Ref. [58] known.

In comparison to previous simulations of nanoindentation, these results are quite good. Simulations of nanoindentation of silver yielded bulk hardness values 4 times larger than experiment [60, 61]. Simulations of nanoindentation of diamond [22] yielded results 10 times harder than experiment. The results for silicon nitride simulations performed by Walsh et al. [15] are a notable exception to this trend; the hardness value obtained from those simulations was in reasonable agreement with experimental data for small indents on silicon nitride.

The quality of the results reported here and in Ref. [15] are likely due to the quality of the interatomic potentials used. The silicon nitride potential used by Walsh has a similar form to that of Equation 3.12 here; the only difference is the silicon nitride potential lacks the $r^{-6}$ two-body term. The parameters for silicon nitride were fit in a similar fashion to those for gallium arsenide.

The purpose of hardness testing is comparative; the values obtained from the test can be directly compared to hardness values for other materials. The hardness value in and of itself has little useful meaning, which is why most experimental hardness tests report hardness on some scale (Vickers, Knoop, Rockwell-B, Rockwell-C, etc.) rather than in the values natural units of pressure. Because of this, it is useful to compare the relative values of hardness for gallium arsenide to silicon nitride for both experimental microhardness and simulated nanohardness to determine if simulated nanohardness can generate a reasonable comparison. Table 5.1 shows this comparison.
Table 5.1: Comparison of relative values for experimental microhardness and simulated nanohardness for gallium arsenide and silicon nitride. In each material, the experimental and simulated indentation were performed on the same crystal face.

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>Si$_3$N$_4$</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.</td>
<td>7.35 GPa (Ref. [58])</td>
<td>31 GPa (Ref. [62])</td>
<td>4.21</td>
</tr>
<tr>
<td>MD</td>
<td>11.7 GPa</td>
<td>54 GPa (Ref. [24])</td>
<td>4.62</td>
</tr>
<tr>
<td>Difference</td>
<td>59%</td>
<td>74%</td>
<td>9.8%</td>
</tr>
</tbody>
</table>

As Table 5.1 indicates, the relative quality of the gallium arsenide simulations results to experiment is nearly identical to that of the silicon nitride results for similar indentation depths reported in Ref. [24]. More importantly, the molecular dynamics simulations reported here and in Ref. [24] accurately represent the relative hardnoses of gallium arsenide and silicon nitride. This indicates that building a ranking standard of simulated nanohardness from simulations of indentation on various materials would be worthwhile, since the relative values could be compared with experiment and that while the simulations do not yield precise hardness values, the values yielded are meaningful. Furthermore, these results indicate that the potentials used in the simulations replicate the complex elastic-plastic behavior of nanoindentation with reasonable accuracy. Currently, indentation simulations are planned for silicon carbide; interatomic potentials of similar quality are available for several other ceramics of note, including indium arsenide, and aluminum oxide.

The initial slope of the unloading curve was fitted to compute compliance in order to obtain the Young’s modulus. A power-law relation was used to fit the slope, in accordance with the methodology given in Ref. [10]. Using this methodology, the Young’s modulus for GaAs in the [110] crystallographic direction was determined to be approximately 99.2 GPa. For comparison, the value of the <110> Young’s modulus
computed from the elastic constants is 121.5 GPa, using the values for the elastic constants given in Table 5.2. The equation for the Young’s modulus of cubic crystals is given by

\[
\frac{1}{E} = \frac{c_{11} + c_{12}}{(c_{11} + 2c_{12})} + \frac{1}{c_{44}} + \frac{2}{c_{11}c_{12}} \left( n_x^2n_y^2 + n_y^2n_z^2 + n_z^2n_x^2 \right),
\]

where \( E \) is the Young’s modulus, \( c_{11}, c_{12}, \) and \( c_{44} \) are the unique elastic constants for a cubic crystal, and the \( n_x, n_y, n_z \) are the unit vectors of the crystallographic direction in which the Young’s modulus is being measured [63]. Our potential for GaAs gives a Young’s modulus value of \( \sim 119.9 \) GPa when measuring the stress induced by a small strain in the [110] direction on a bulk system.

<table>
<thead>
<tr>
<th>Table 5.2: Elastic constants for GaAs at 300 K, from Ref. [58]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_{11} )</td>
</tr>
<tr>
<td>( c_{12} )</td>
</tr>
<tr>
<td>( c_{44} )</td>
</tr>
</tbody>
</table>

5.4 Analysis of pileup region

As it is observed in both microindentation experiments and the simulations performed on silicon nitride by Walsh et. al. [24], material from the damaged region was deposited on the surface of the GaAs substrate in essentially non-contiguous, irregularly shaped lumps at each face of the indenter, as illustrated in Figure 5.8. This pileup was suppressed along the indenter diagonals in our simulations, consistent with the observations reported in Ref. [24]. For silicon nitride, the material in the pileup region was determined to have undergone solid-state amorphization; a similar analysis was
Figure 5.8: Illustration of pileup on the surface. The red atoms are pileup material, yellow atoms are surface atoms, and white atoms are indenter atoms. The view is perpendicular to one indenter face; the suppression of pileup along the indenter diagonals can be seen in the lack of pileup material at the edges of the faces. Picture courtesy of Andy Haas, NAVO Major Shared Resource Center, Stennis Space Center, MS.

performed on the GaAs system studied here to determine if the deposited GaAs in the pileup region had also undergone solid-state amorphization.

To compare the pileup with amorphous gallium arsenide (a-GaAs), we first computed the density of the pileup material. Since there were four noncontiguous regions of pileup, one for each indenter face, and each of these regions was irregularly shaped, the density of the pileup material was measured by taking small orthorhombic volumes in the pileup region and counting atoms within these volumes. The total number of atoms of each atomic species selected by these volumes and the total volume selected were summed. The total number of atoms of each species was then multiplied by the appropriate atomic mass. The density was then simply calculated from these total masses and the volume that contained them. By this method, the average density of the pileup region was determined to be 4.31 g/cm³. In comparison, the bulk crystalline density of GaAs is 5.31 g/cm³.
While no experimental data on amorphous GaAs at this density exists for comparison, the interatomic potential for GaAs used in these simulations has been compared to experimental results for amorphous GaAs at higher densities [38]. The potential reproduces key features of amorphous GaAs, including bond angle distributions, x-ray scattering structure factor, and phonon density of states. Since the potential gives a good description of amorphous GaAs, we can use a simulated bulk GaAs system at the same density as the material in the pileup for comparison.

For this comparison, a small (4,096 atoms) bulk crystalline GaAs system was created and then amorphized. Figure 5.9 illustrates the schedule for preparation of this

![Simulation schedule for preparing GaAs amorphous system. The system was determined to be melted when the mean square displacement curve for atoms in the system drifted steadily upwards over time.](image)

Figure 5.9: Simulation schedule for preparing GaAs amorphous system. The system was determined to be melted when the mean square displacement curve for atoms in the system drifted steadily upwards over time.
bulk amorphous system. The system was created with a temperature of 300 K, and was then heated to 1100 K. The heating was accomplished by scaling the particle velocities to heat the system by 200 K and then allowing the system to thermalize over 2000 timesteps. This process was repeated until the system reached 1100 K. The MD simulation cell was then expanded in all directions, preserving the periodic boundary conditions, at an expansion rate of 1% every 2000 t until the system reached a density of 4.31 g/cm³. The heating then continued at the same rate until the system melted, as determined by the mean square displacement of the particles in the system. The molten liquid was allowed to thermalize for 50,000 t, then was cooled slowly to 0 K.

Bond length and bond angle distributions (Figures 5.10 and 5.11, respectively.) were calculated for both the pileup region and the bulk amorphous system. The comparison of the two systems indicates that the pileup region is structurally similar to amorphous GaAs.

![Graph](image)

Figure 5.10: Bond length distribution comparison between the pileup material (red line) and bulk amorphous GaAs (blue line).
Figure 5.11: Bond angle distribution comparison. The red lines indicate data from the pileup region, the blue lines are bulk amorphous GaAs. The bond angle data indicate that the pileup material is structurally similar to the bulk amorphous GaAs system.

The possibility of a phase transition from a zinc-blende crystal structure to a rocksalt crystal structure was also considered. Coordination number distributions were computed to look for this zinc-blende (4-fold coordinated) to rocksalt (6-fold coordinated) transition. Simulations on GaAs nanocrystals using the same potential indicate that the onset of the transformation is at approximately 16 GPa [64]. Since the maximum hydrostatic pressure under the indenter never exceeded 4 GPa, no transition
was expected, and the coordination number distributions did not contain any peak that would indicate the presence of 6-fold coordinated GaAs.

5.5 Dislocation analysis

Figure 5.12 shows a snapshot of the system at the peak load of 0.59 µN, with only atoms exhibiting a large (~0.5 eV) deviation from equilibrium potential energy visible. In this image, there is a suggestion of a continuous defect terminating at the GaAs surface and continuing downward to the tip of the damage region. We therefore wanted to

Figure 5.12: High-energy atoms underneath the indenter. Note the linear defect extending downward from the top surface. Green atoms are arsenic, red atoms are gallium.
determine to what degree the energy of the indentation was dissipated by amorphization versus the generation of dislocations. To accomplish this, we attempted to characterize the nature of the deformation in the substrate.

Simply selecting atoms on the basis of their potential energy is not sufficient to differentiate between the atoms in the damaged region adjacent to the residual pockmark and atoms that bounded dislocations. We therefore implemented the centrosymmetry method of Kelchner et al. [65], to attempt to separate these atoms from other high energy atoms in the deformed region. This centrosymmetry method was shown to be quite sensitive to defects in FCC metals.

What the centrosymmetry parameter measures is the local non-affine deformation of the crystal lattice at a lattice point. Since elastic deformations are both small and affine, i.e., the deformation can be obtained by applying an affine transformation such as shear or compression to the crystal, the centrosymmetry parameter highlights regions of non-elastic deformation. These include linear dislocations as well as other defects such as stacking faults and surfaces. In simulations on FCC metals, the parameter clearly separated a partial dislocation loop from the stacking fault it borders [65]. In calibrating the method for GaAs, we were able to clearly differentiate between low index surfaces, i.e., \{100\}, \{110\}, and \{111\}, on this basis.

The centrosymmetry method consists of summation of the squares of the vector sums of nearest-neighbor vectors. In Figure 5.13, this scheme is illustrated for a simple cubic system. The nearest-neighbor vectors are labelled 1 – 6, and with this convention, the centrosymmetry parameter is given as
Figure 5.13: Illustration of the centrosymmetry labelling on a simple cubic lattice.

\[ P = \left\{ \mathbf{R}_i + \mathbf{R}_{i+} \right\}^2, \]

where \( P \) is the centrosymmetry parameter, and the \( \mathbf{R}_i \) are the nearest neighbor vectors.

From dimensional analysis, it is clear that the centrosymmetry parameter has units of area. Considering a simple defect, such as a slip or an edge dislocation, which are typically characterized in terms of lattice constants or fractions thereof, there is an implicit dependence of the centrosymmetry parameter upon the lattice constant of the system being studied. It may be convenient to express the parameter normalized by the square of the lattice constant, thus creating a dimensionless parameter that could thereby be compared across different materials. The results in this dissertation do not employ this normalization.
Since GaAs has a zinc-blende structure, we applied the centrosymmetry to one sublattice, typically the As sublattice, as the zinc-blende crystal is essentially two interlocking FCC lattices offset by \( \frac{1}{4} \quad \frac{1}{4} \quad \frac{1}{4} \) the lattice constant. We created a reference state from the undamaged system, mapping the nearest neighbors of each atom on the sublattice. This reference system was used to identify which atoms to use in the calculation after the damage had taken place. Atoms that had undergone catastrophic motion, or whose neighbors had undergone catastrophic motion, typically had centrosymmetry values that were meaninglessly large, and thus for clarity we set an upper limit on the centrosymmetry value. Any centrosymmetry values larger than 100 Å² were set to be equal to 100 Å² in the results reported here. The limiting value of 100 Å² was determined from the distribution of centrosymmetry values. Above 100 Å², the centrosymmetry distribution consisted only of single incidences of various values of the centrosymmetry parameter.

The application of the centrosymmetry method to the GaAs system yielded poor results. While indenter damage was typically indicated by large centrosymmetry values, the atoms just inside the pockmark were not statistically separable from the atoms surrounding the dislocation cores on the basis of centrosymmetry parameter alone. Figure 5.14 shows a snapshot of the system with the atoms colored by centrosymmetry and with atoms having a centrosymmetry parameter near 0 Å² removed so that the details of the high centrosymmetry parameter region around the indenter will be visible.

Although the centrosymmetry analysis did not provide a decisive means to preferentially select atoms surrounding a dislocation core, slices parallel to the surface, such as that in Figure 5.15, showed the characteristic “lattice half-plane” of edge
Figure 5.14: Atoms with high centrosymmetry parameter. The linear defect observed in Figure 5.12 is not clearly highlighted here, illustrating the difficulty in differentiating the dislocation loops from the damage. All values of centrosymmetry parameter higher than 100 Å² were set equal to 100 Å² for clarity. Picture courtesy of Andy Haas, NAVO Major Shared Resource Center, Stennis Space Center, MS.

dislocations. By following these from slice to slice from the surface to the tip of the damaged region, we determined that the dislocations did terminate on the edges of the residual pockmark at the surface and in the damaged region near the tip of the residual pockmark within the substrate.

One obvious explanation for the failure of the centrosymmetry method to provide adequate results stems from the analysis in Section 5.4 and is based on an essentially geometric argument. Since the amorphization that takes place under the indenter necessarily implies a non-elastic deformation of the FCC sublattice, the onset of amorphization or liquefaction would be accompanied by a distribution of centrosymmetry...
values, since the degree of this non-elastic deformation would vary with the degree of amorphization. Furthermore, since this deformation would be small at the onset of amorphization, it would tend to obscure other peaks representing similarly small deformations. Dislocations are typically due to small (~1 lattice constant) deformations. Therefore, the onset of the amorphization due to the indenter could obscure the peaks due to dislocations.

Figure 5.15: A z-plane slice at 20 Å below the substrate surface, illustrating the presence of dislocations. This image depicts a region 100 Å x 100 Å. Note that only As atoms are shown. Color indicates centrosymmetry parameter values.

A third criterion explored in the attempt to highlight the dislocations was coordination number. Inspection of the atomic positions in planes such as shown in
Figure 5.15, with the atoms labelled by coordination number instead of centrosymmetry, seemed to indicate that some atoms surrounding the dislocation core were overcoordinated. While it was clear from inspection that this criterion was not sufficient to highlight the dislocations, several filters combining coordination number with other criteria were employed. Various combinations of parameters with coordination, including potential energy and centrosymmetry, were tested to determine whether the dislocation atoms could be distinguished by such a combination. No combination of parameters was found that highlighted the dislocation atoms clearly.

5.6 Fracture of the substrate

The simulation results reported on silicon nitride by Walsh et al. [15] showed that microcracking underneath the surface occurred during the indentation process. We were interested in determining whether similar cracking occurred in GaAs, and thus we analyzed GaAs for evidence of microcracking. Microcracking is normally indicated by residual wells of tensile stress remaining in the substrate at the boundary of the zone of plastic deformation after the indenter was fully unloaded.

We generated a series of slices perpendicular to the z axis and plotted the average stress in voxels on each slice. Figure 5.16 is such a slice, showing the voxel-averaged hydrostatic pressure on a slice 20 Å below the indenter surface. The voxel dimensions were equal to that of the GaAs unit cell, 3.997 Å x 5.653 Å x 3.997 Å. As discussed in Section 3.4.4, the definition of pressure used in these simulations is the virial definition, and the stress in each voxel is the sum of the virial for each atom contained within the voxel (see Equation 3.33).
Figure 5.16: Pressure distribution on a slice 20 Å below the surface of the GaAs substrate. No tensile wells that would indicate the presence of microcracking or pore formation are present.

We found no tensile wells in the simulated GaAs system that would indicate the presence of microcracks or pores. While the voxels containing atoms around dislocation cores exhibited non-zero pressure, the extent of these regions was small compared to the regions observed in Ref [15]. The lack of microcracking was corroborated by looking at the atomic planes as well, such as the plane shown in Figure 5.17. While disordering and dislocation emission was observed, as discussed in Section 5.5, there was no sign of microcracking nor was there indication of pore formation that would be suggestive of microcracking.
Figure 5.17: Atomic positions on a slice 20 Å below the surface. Atoms are colored by their potential energy. For clarity, only arsenic atoms are shown.

These results indicate that the energy of the indentation was completely dissipated by the amorphization and dislocation formation described in Sections 5.4 and 5.5. It is possible that at larger indentation depths and commensurately longer times that cracking would occur, either due to the cumulative effect of dislocation pileup or simply due to the larger stresses the indenter would induce in the substrate.
CHAPTER 6

INDENTER-SUBSTRATE ADHESION

6.1 Motivation and system construction

Adhesion between the indenter and substrate is an important phenomenon in experimental nanoindentation and has been studied with molecular dynamics. Landman and Luedtke studied an effect of these interactions, the so-called tip-surface jump to contact phenomenon, in molecular dynamics simulations of nickel and gold [20]. In essence, they found that as the tip approaches the surface, within a few angstroms, either the top layer of the surface jumps up to meet the tip or conversely the tip undergoes deformation to contact the surface. Which of these two occurrences take place is governed by the relative Young’s modulus of the two materials.

This effect was also seen for silicon nitride in the simulations performed by Walsh et al. [24]. In these simulations, it was found that making small indents at loads less than the yield point in silicon nitride would, as expected, leave no residual damage to the substrate. Some of the surface atoms, however, would be pulled up and out of their equilibrium positions by the indenter.

We studied the effects of tip-surface adhesion in GaAs, with a system prepared in the following fashion. A slab of dimensions 455 Å x 452 Å x 200 Å was generated on 128 processors using a similar decomposition to that described in Section 5.2. The slab was then heated to 300 K, following the same schedule outlined in Figure 5.4. Again, the (110) surface of GaAs was indented, and periodic boundaries were maintained in the
and [001] directions, corresponding to the x and y axes respectively. These simulations were performed on the Cray T3E at the Naval Oceanographic Office Major Shared Resource Center.

The model of the indenter in the adhesion simulations was geometrically similar to the indenter described in Section 5.1, the only difference being that the tip was truncated to leave a small flat surface. While the indenter atoms were held rigid as before, the attractive two-body potential components, including the screened Coulomb interaction, the charge-dipole interaction and the van der Waals interaction, between the indenter and substrate atoms were turned on again. For simplicity, the values used in the indenter potential were identical to those for the substrate. Since the two atomic species, gallium and arsenic, had non-zero charges, care had to be taken to make sure that the flat indenter surface was charge-neutral. After the surface was cut, the stoichiometry of the surface was tested to insure charge neutrality.

Additionally, to reduce the load imbalance due to the indenter, the solid square-based pyramid geometry used in the simulations described in Chapter 5 was modified to be a square-based pyramidal shell approximately 15 Å thick. This removed atoms from the center of the indenter that would not interact with any non-indenter atoms. It also reduced the load imbalance by reducing the variation in the number of atoms mapped to each processor; with a solid indenter, processors near the center of the system, where the indenter was thickest, would have more atoms resident than processors near the boundaries of the system.

For the adhesion simulations, only short traversals were used. Three loading schedules were of interest: tip approach and contact, contact and small indent, and
indentation beyond the yield point. Figure 6.1 illustrates the logic of the adhesion schedule. In each subsequent traversal, a configuration from the prior traversal is used as the starting point. This allowed us to avoid repeating portions of the traversal unnecessarily. The traversal to a depth of 7.5 Å thus began at the peak depth of the tip approach and contact traversal, i.e., 0 Å.

In the loading cycle, the indenter was moved approximately 0.5 Å every 250 timesteps. This velocity is identical to that used in the simulations described earlier in

![Flowchart](image)

Figure 6.1: The schedules for the adhesion simulations. The indenter velocity was the same 1 Å/500 t rate described in Section 5.1.
Chapter 5. Because it was found that the quality of the load-displacement data was sensitive to the presence of the holding phase, we introduced a holding phase after every 0.5 Å of indenter motion instead of after every 1 Å of indenter motion. In these simulations, the holding phase was 1000 timesteps in length.

6.2 Load-displacement curves

As Figure 6.1 illustrates, we simulated three traversals representing tip approach with contact, a shallow indent, and an indenter beyond the yield point. In each subsection below, the load-displacement curves for the corresponding traversals are given, with a discussion of the key features of each. A detailed analysis of the yield point phenomenon is given in Section 6.3.

6.2.1 Tip approach with contact

The first situation of interest is the tip approach with contact. The load-displacement curve obtained from this simulation is given in Figure 6.2. The key feature of this curve is the attractive well that appears just before contact. This is consistent with the results of previous simulations [24]. The onset of the attractive well came when the bottom of the indenter came within approximately 6.5 Å of the surface, corresponding to the force cutoff length of the model. The minimum force observed in the attractive well was \(-1.1 \times 10^{-3}\) μN at an indenter-surface separation of 6.1 Å. The indenter-surface interaction crossed back in to the repulsive regime at a separation of 5.9 Å. The separation was measured using the same methodology as given in Section 5.3 the separation or depth being defined as the difference between the average position of the surface layer before indentation and the minimum position along the z-axis of any atom in the indenter. Figure 6.2 gives this initial load-displacement relation.
Figure 6.2: Load-displacement relation for tip approach. The attractive well appears as the indenter atoms begin to interact with the surface, and disappears once the lowest layer of indenter atoms are close enough to the surface for the short range repulsion to dominate.

The depth of the attractive well for GaAs is shallower than the well for silicon nitride as given in Ref. [24] by almost an order of magnitude. This simply reflects the generally lower cohesive energy that a gallium arsenide crystal has compared to silicon nitride. Also of importance is the difference in the apparent position of the attractive well in terms of the indenter depth as compared to the results of Ref. [24]. This difference is due to a different convention for defining indenter displacement than the one given in Section 5.3. According to this definition, the indenter and the surface would start to interact as soon as the calculated depth was within the force cutoff. The definition of depth provided in Ref. [24] puts the point of zero depth where the load becomes positive.
or in the case of the adhesion simulations, at the cross-over point between the attractive and repulsive regimes [15].

6.2.2 Indent below the yield point

The next cycle was to a depth of 7.5 Å. This simulation was continued from the simulation of tip approach. The system configuration at the peak loading during the first cycle was saved and the simulation was restarted at this point. Once the indenter reached a depth of 7.5 Å, the system was unloaded.

Figure 6.3 shows the load-displacement curve for this traversal. From the lack of hysteresis in this curve, it is apparent that the yield point was not reached, despite a slight shoulder in the curve which otherwise might indicate the onset of plastic deformation.

![Load-displacement curve for traversal to 7.5 Å depth. No hysteresis is observed.](image-url)
The failure of the unloading curve in Figure 6.3 to retrace the loading curve exactly is an effect of the transient forces in the system due to the loading; in systems where the holding phase happened less frequently or where the holding phase was shorter, this effect was larger than the slight deviation observed here.

A snapshot of the system after unloading (Figure 6.4) shows that while atoms have been pulled from the surface, there is no residual damage due to the indenter. This is corroborated by a plot of atom positions in the layer underneath the surface (Figure 6.5). This lack of residual damage supports the evidence of the load-displacement curve that the yield point had not yet been reached.

Figure 6.4: Surface after 7.5 Å traversal. Note that while some atoms have been pulled from the surface, there is no residual damage in the system. This indicates that the surface damage was due solely to tip-surface bonding, as discussed in Section 6.4. Red atoms denote gallium, green atoms denote arsenic, and the indenter atoms have been removed for clarity.
6.2.3 Indent beyond the yield point

The last traversal was to a depth of 18.3 Å. Figure 6.6 shows the load-displacement relation for this traversal. This curve clearly shows the characteristic hysteresis of loading past the yield point. There is a shoulder at a depth of about 8.5 Å that appears to indicate the onset of plastic deformation. Unloading the system from that point gives the load-displacement relation shown in Figure 6.7. The unloading curve from this point shows a hysteresis, indicating that this is the yield point. The load at the shoulder is 0.6 µN.
6.3 Residual damage to the substrate

We looked at the surface atoms after the indenter was unloaded from a depth of 18.3 Å. There was significant pullout of material due to the indenter-substrate interaction as is shown in Figure 6.8. The extent of the catastrophic damage, i.e., where significant atomic rearrangements are observed, is limited to the four atomic layers underneath the surface (~5 Å). Analysis of the layers under the surface revealed active slip systems and the presence of dislocations.
Figure 6.7: Load-displacement relation after unloading from a depth of 8.5 Å. The red curves are the full 18.3Å traversal as shown in Figure 6.6, while the blue curve is the unloading curve from 8.5 Å. While the curve seems to retrace the loading curve for a portion of the unloading cycle, the indenter reaches the point of zero load before the indenter is fully withdrawn. The loading curve exhibits a slight anomaly in the data points just prior to the unloading, indicating the onset of plastic deformation. The yield point load is 0.6 µN.

Figures 6.9(a), (b), and (c) show (110) planes approximately 10 Å, 18 Å, and 28 Å below the surface respectively. In these slices, we have restricted the view to a 200 Å x 200 Å region centered under the centroid of the indenter. In Figure 6.9(a), we see the formation of dislocations clearly; the regions of high deformation are highlighted. At 28 Å below the surface, there is only little deformation present. Note that in 6.9(a) and (b), one region of deformation is located in approximately the same x-y position, near the
Figure 6.8: Top three layers of the substrate. Note the material that adhered to the indenter and was deposited on the surface, as well as the disruption in the definition of the layers. Purple atoms denote gallium, red atoms denote arsenic. The indenter atoms have been removed for clarity.

bottom of the figures in each case. This is suggestive of onset of a dislocation similar to what was observed in the simulations in Chapter 5. A plot (Figure 6.10) of a small volume (30 Å x 30 Å x 60 Å) underneath the surface centered on that green-shaded damaged region at the bottom of Figures 6.9(a) and (b) suggests that the damage has some orientation in the z direction, perhaps a loop, and thus is similar to the dislocations observed in Chapter 5.

In contrast to the simulations reported in Chapter 5, here there is an insignificant amount of plastic flow observed. Consequently, there is no indication of the onset of solid-state amorphization. This indicates that the initial stages of plastic deformation are characterized by the formation of dislocations. As the compressive stresses underneath the indenter increase, the substrate will then amorphize and flow, creating the pileup regions described in Section 5.4.
Figure 6.9(a): A (110) plane at a depth of 10 Å below the surface. Regions of plastic deformation consistent with the formation of dislocations highlighted. The region near the bottom of the image is located in roughly the same x-y position as a similar region in Figure 6.9(b). The 30 Å x 30 Å area that is the projection of the volume plotted in Figure 6.10 corresponds to the square that encloses the green circle highlighting the region.

Figure 6.9(b): A (110) plane at a depth of 18 Å below the surface. This the maximum depth the indenter reached during the traversal. Regions of deformation are highlighted.
Figure 6.9(c): A (110) plane at a depth of 28 Å below the surface. The damage in this plane is small compared to that shown in Figures 6.9 (a) and (b).

Figure 6.10: A projection onto the y-z plane of a 30 Å x 30 Å x 60 Å volume centered on a damaged region from Figures 6.9(a) and (b). The black line shows position of the surface and the blue lines are the positions of the slices for Figures 6.9(a), (b), and (c). Only atoms whose deviation from equilibrium potential energy is greater than 0.5 eV are shown.


6.4 Elastic recovery of the surface

For indents within the elastic regime, in this case, with depths less than 8.5 Å, a significant recovery was observed. Figure 6.11(a) below shows the surface underneath the indenter at full loading, with the indenter atoms removed for clarity. The surface is disordered in the region of the dimple. Figure 6.11(b) shows the surface after the indenter has been completely unloaded. The surface has relaxed and recovered from the damage. Note that there is some disordering in three locations; these locations

![Image](image_url)

Figure 6.11: Substrate surface with the indenter at a depth of 7 Å. The view direction is along the $\overline{1}10$ direction. The indenter atoms have been removed to reveal the details of the surface. The center of the dimple is flat and remains relatively ordered, while the sloping regions at the edges of the dimple exhibit disordering.
correspond with the corners of the indenter and the disorder consists of atoms being pulled from the surface of the substrate. The damage does not, however, extend any further below the surface; inspection of atomic positions in slices under the surface reveals an insignificant degree of disordering.

Since the process of bond formation and breaking is a thermodynamically irreversible process, i.e., the process is associated with a finite amount of work done on the system, whereas the elastic deformation of the subsurface layers is reversible, this indicates that the work done on the substrate by the indenter is limited to the atoms with which bonds are formed. Since it is clear from Figure 6.11 that there is no large scale disruption of the surface layer, the only tip-surface bonds formed would be with the surface layer of atoms.

The atoms pulled out of the surface layer as shown in Figure 6.12 are located underneath the corners of the lowest indenter plane, the one in contact with the surface, as can be seen from the positions of the indenter atoms in the figure. These corners correspond to regions of high potential energy, since the atoms there are undercoordinated compared to the bulk and a surface. If tip-surface bonding were the cause of the atoms being pulled from the surface, it would follow that regions of the surface beneath the most undercoordinated indenter atoms would be the preferred locations for the pullout to occur.
Figure 6.12: Substrate surface after indenter withdrawal. While the surface has healed itself, three points along the surface exhibit pullout of surface atoms. These points correspond roughly to corners of the lowest plane of indenter atoms. Indenter atoms are shown in purple. Red atoms are gallium, green atoms are arsenic.
CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

We have performed the first simulations of the nanoindentation of GaAs. While the general approach was validated by earlier simulations [20, 24, 66], the mechanical properties calculated from these simulations were compared with the experimental values. We found both the calculated hardness to compare well with experimental microhardness data for the identical crystal face and the calculated Young’s modulus to compare well with the value obtained by elasticity theory from the experimental elastic constants.

It was found that the relative quality of the hardness results for gallium arsenide as compared to the silicon nitride results of Ref. [24] indicate that molecular dynamics simulations accurately reproduce the relative hardnesses of the two materials as compared to experiment. This is the first step in building a reference standard for simulated nanohardness, to which values from the simulations of other ceramics, including silicon carbide and alumina can be added. This result also indicates that semiempirical potentials of the form used here accurately depict the complex elastic-plastic behavior that nanoindentation measures.

We found that GaAs undergoes deformation during indentation both by a process of solid-state amorphization and flow, but also by the formation of dislocation loops terminating on the residual damage. A centrosymmetry method was used to analyze
these dislocations; it was found that such a technique is insufficient to separate the
dislocation loops from the regions of amorphized material along the surface of the
residual pockmark. Subsurface cracking and pore formation were not observed in these
simulations, in contrast to earlier simulations on silicon nitride by Walsh et al. [24].

Simulations modelling adhesive effects between the indenter and substrate were
also performed. In these simulations, it was found that the initial stages of plastic
deformation are due to the formation of dislocations in the substrate underneath the
indenter. Significant deformation of the top layer of the substrate was also observed in
both after small indents and indents past the yield point of the system.

The hysteresis associated with the “jump to contact” phenomenon was observed
in traversals where the tip came close to the surface without contact. This irreversible
behavior is consistent with previous simulations [24] and is caused by the formation and
breaking of tip-surface bonds. The anomaly in the load-displacement curve that indicated
the onset of plastic deformation occurred at a load of 0.6 μN and a depth of 8.5 Å. Since
the initial plastic deformation was due to dislocations in the substrate, rather than by the
microcracking observed by Walsh [24], this load-displacement anomaly is not as clear as
that observed in silicon nitride.

7.2 Directions for future work

The results of these simulations have raised several important questions. The first
is whether cracking will occur under higher stresses. Currently, a larger (~65M atom)
GaAs indentation is in progress in order to study this and other phenomena. Another
question that arises from these results is the nature of the crossover in the types of plastic
deformation that occurs, from dislocation formation to solid-state amorphization and
theoretically to microcrack formation. It would be interesting to explore this in more
detail, including the calculation of fracture toughness from any cracks that form. Further
exploration of the effects due to adhesion would also be useful, particularly how the tip-
surface bonding affects the damaged region after the onset of amorphization.

Another direction of study is to simulate the nanoindentation of multilayered
systems. Simulations have been performed here on silicon-silicon nitride systems and
gallium arsenide-indium arsenide systems to study the mechanical properties of
multilayered systems and quantum dot assemblies. The effects of thin films on substrates
and vice versa are well known experimentally and studying the atomistic behavior behind
these effects might prove to be useful.

Nanoindentation data, including calculated Young’s modulus, exist for
amorphous silicon carbide [67]. Our research group has developed an excellent potential
describing silicon carbide [68, 69] and thus it would be quite simple to perform a
simulation roughly equivalent to these on an a-SiC system.

One last possibility for future work would be to measure the friction of the
indenter sliding across a surface. Given the indenter logic currently in place, it would be
straightforward to implement such a traversal. To obtain meaningful data on friction
coefficients, the indenter update logic would have to be altered slightly. As discussed in
Chapter 5 and illustrated in Figure 5.1, the indenter atoms are kept at a constant position
until update, whereupon they are moved some small distance. The reaction force of the
substrate pressing back against the indenter is then measured. For friction simulations, it
is desirable to maintain a constant small load [57]. The indenter logic could easily be
altered to use the measured force as the input to control the motion of the indenter, in an
analagous fashion to a mechanical control system. With this technique, a wide range of tribological phenomena could be investigated.
REFERENCES


VITA

Francis Brent Neal, Jr. was born on December 10, 1973, in Rockingham, North Carolina. Brent graduated from the North Carolina School of Science and Mathematics in Durham, North Carolina, in June 1992 and enrolled in the College of Physical and Mathematical Sciences at North Carolina State University.

During his enrollment at North Carolina State University, Brent was privileged to work with Dr. John C. Russ in the field of image analysis and computer-assisted microscopy and with Dr. Donald W. Brenner in the field of computational materials science. After transferring to the College of Engineering, he graduated from North Carolina State University with a Bachelor of Science degree from the Department of Materials Science and Engineering in May 1996.

In August 1996, Brent entered the doctoral program at Louisiana State University and was awarded a National Science Foundation Graduate Research Traineeship. He joined the Concurrent Computing Laboratory for Materials Simulations at that time. He was awarded a Master of Science in physics from Louisiana State University in December 1998 and enrolled in the Master of Science in Systems Science Program as part of a dual-degree opportunity offered by Louisiana State University.

He lives in Baton Rouge, Louisiana, with his wife, Sarah, and currently plans to enter the private sector after receiving the degree of Doctor of Philosophy in August 2002.