B. TECH. PROJECT REPORT On Mechanics of Shear Transformation Zone in metallic glasses using Density Function Theory calculations

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Mechanics of Shear Transformation Zone in metallic glasses using Density Function Theory calculations

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CANDIDATE'S DECLARATION

We hereby declare that the project entitled "Mechanics of shear transformation zones in metallic glasses using Density Functional Theory calculations" submitted in partial fulfillment for the award of the degree of Bachelor of Technology in 'Mechanical Engineering' completed under the supervision of Dr. Indrasen Singh, Assistant professor, Dept. of Mechanical Engineering, IIT Indore is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

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CERTIFICATE by BTP Guide(s)

It is certified that the above statement made by the students is correct to the best of my knowledge.

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Preface

This report on "Mechanics of shear transformation zones in metallic glasses using Density Functional Theory calculations" is prepared under the guidance of Dr. Indrasen Singh

This report is to summarize the results of the work I carried out on the study of mechanics of Shear Transformation Zones (STZ) in metallic glasses using Density Functional Theory (DFT) Calculations. DFT is an ab initio method to study electronic problems and thus provides much accurate results than the empirical interatomic potentials. In this work, I have made an attempt to describe the objectives, motivation, methodology and analytical results to obtain the design parameter associated with Shear Transformation. Shear transformation being the major failure mechanism in the amorphous metallic glasses, understanding the accurate design parameters aids in the design process. Thus, the friction parameter associated with the Mohr Coulomb yield criteria have been found for the Copper and Zirconium based systems using DFT-FE code and validated using advanced semi empirical potential calculations

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Abstract

Metallic glasses are materials with exciting mechanical attributes which promise to make up excellent materials for engineering applications. However, the design through any material, demands the knowledge of the failure mechanisms and strength under loads. This particular field is an active area of research for the metallic glasses, the failure mechanisms for which have been debated since their discovery.

The contemporary research points out to shear transformation process leading to formation of shear transformation zones (STZs) and shear bands as a fairly accepted mechanism of failure in amorphous metallic glasses. In this process atoms cooperatively accommodate the shear strain and transform their positions, propagating the distances further to create multiple STZs and coalesce them to form a shear band.

In the current work a miniature model of a unit shear transformation has been studied with reference to the published literature cited in the chapters ahead. Molecular static simulations have been performed on various deformed configurations and the computational data has been processed to get the friction parameter associated with the Mohr Coulomb yield criteria which is an accepted failure criterion governing the failure mechanism of metallic glasses. The work initially replicates the published results using empirical potentials and then ab initio simulations are carried out to compare the results with the earlier results.

In the chapters below the methodology and the results are elaborated, conclusions are drawn based on the work and the scope of future work is delineated.

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CHAPTER 1

INTRODUCTION TO METALLIC GLASSES AND LITERATURE REVIEW

1.1 Characteristics of metallic glasses and application

Developments of new engineering materials are always a key challenge and an important topic for material researchers during last few decades. Metallic glasses (MGs) are amorphous or non- crystalline and asymmetric nature but are typically opaque, are not brittle in general. Historically, metallic glasses were reported in 1960 by Klement et al. [1] during their classic rapid-quenching experiments on Au-Si alloys. During the last six decades, numerous reports [2], review articles [3-8], and textbooks [9 and 10] have been reported by material researchers with great amount of attention and effort to understand the technological development of MGs and exploit their characteristic/superior properties and potential applications.

Besides the mechanical properties of MGs, Pampillo [11] and Argon [12] specifically focused upon fundamentals and mechanisms of deformation and fracture through their classic review articles. MGs are attracted as emerging structural materials among the material researchers due to their impressive mechanical, chemical and physical/functional properties [2, 13-15]. Further rigorous works discussed the correlation between their structure and material properties [16 and 17] and shear banding phenomena [18 and 19].

Atoms in a MG are randomly packed without any long-range order, therefore it give fundamentally different deformation mechanisms which allow MGs extreme high strengths (~10 times more than that of Aluminium), low density, low Young's modulus (high yield strain and resilience), high hardness, high toughness, resistance to wear and corrosion, superplasticity at high temperatures (ability to be formed like plastics) and moderate to high fracture toughness, high flow stress, and high ductility. MGs have higher Poisson's ratio which are more likely achieve better plasticity and toughness. In addition, MGs show high compressive yield strength on the order of several GPa at room temperature [20] and also it exhibit larger elastic strain up to ~ 2-3 %, with elastic moduli comparable to those of crystalline alloys. However, due to the poor understanding of atomic configuration and flow mechanism in MGs, the physics behind such connections is still under study.

These unique combinations of superior material properties allow MGs to use in tremendous application areas such as structural (high torque geared motor parts, high corrosion resistant coating plates, kinetic energy penetrator rods, razor blades and different kinds of springs and watch cases), electrical and electronics (casings of electronic devices, tape recorders heads, transformer core material, cryo thermometers, magnetoresistive sensors, accurate standard resistances and computer memories), nuclear reactor (containers for nuclear waste disposal and magnets for fusion reactors, and inner surface of the reactor vessels), health and biomedical (biomedical instruments such as endoscope parts, cutting and making surgical instruments and prosthetic materials for implantation in human body), magnetic (electromagnetic shielding plates, soft magnetic choke coils, soft magnetic high frequency power coils, magnets for fusion reactors and high magnetic fields and magnetic levitation effect) and also in sports (tennis racquet frames and golf club heads).

Safe deployment of MGs in wide range of structural applications requires an appropriate understanding of their mechanical behavior in terms of deformation behavior and failure criteria. Mechanics of modern materials are established by physicists and materials scientists based on the effect of work-hardening, dislocations, grains, grain boundaries and shear deformation. However, especially MGs along with some other materials show work-softening effects instead of workhardening. The deformation mechanisms of amorphous such as MGs are extremely challenging due to the lack of conventional mechanisms in MGs which can carry plastic deformation. In addition, there are several theoretical models proposed in order to investigate the atomic mechanism of inelastic, elastic and plastic deformation of various amorphous alloys based on local structural rearrangement of atoms. However, there are hardly any experiments or reliable theoretical models to understand atomic process of elastic and plastic deformation of such amorphous metals.

1.2 Mechanism of plastic deformation and failure

According to theory of plastic flow in Metallic Glasses (MGs) [31-33], the basic/fundamental unit of plasticity or deformation in amorphous metals is termed as shear transformation zones (STZs). An STZ is a fundamental flow defects but not a structural defect in an amorphous metal. An STZ is a small cluster of ~10-100 [34] randomly close-packed atoms that spontaneously and cooperatively reorganize under the action of an applied shear stress. In the simulation of STZs a wide variety of simulated compositions and empirical inter-atomic potentials are used and suggested that STZs are common to deformation of all amorphous metals even though the details structure, size and energy scales of STZs may vary for different amorphous materials [4]. As the exact nature of local atomic deformation in MGs is not fully resolved, a 2D schematic of Fig. 1.1(a), originally proposed by Argon and Kuo [35] on the basis of an atomic-analog bubble-raft model which shows how an STZ can accommodate a small increment of shear strain. The event depicted in Fig. 1.1(a) has been referred to as a "flow defect", a local inelastic transition and "STZ". The continued propagation of shear strain occurs by a process of self-assembly: the operation of one STZ creates a localized distortion of the surrounding material, and triggers the auto catalytic formation of large planar bands of STZs, commonly called shear bands.



Fig 1.1: Failure mechanisms in Metallic glasses

An alternative way, the plastic flow mechanism in MGs is also given by classical "free-volume" model [36 and 37] and applied for glass deformation by Spaepen [32]. This model essentially views deformation as a series of discrete atomic jumps in the glass, as depicted in Fig. 1.1b, these jumps are obviously favored near sites of high free volume which can more readily accommodate them. Even though, it is not clear why local diffusive jumps would be biased by shear stresses and a single atomic jump does not accommodate shear strain. But also, the free volume model introduces a simple state variable to the problem of glass deformation, and allows constitutive laws to be developed on the basis of competing free volume creation and dissolution through a simple mechanism.

1.3 Review of experimental work related to strength of metallic glasses

One important consequence of shear deformation in amorphous metals is yield criterion which exhibit a dependence not only upon the maximum shear stress, but also upon the hydrostatic pressure or normal stress acting on the shear plane. The von mises and tresca criteria suggest symmetric strength in compression and tension. However, MGs have displayed asymmetric yield behavior in several experimental studies [44, 53 and 55] and also the failure behaviors of MGs are quite different because of their unique mechanical behaviors which made challenges with the use of traditional experiences and theories. Hence, the Mohr Coulomb yield criteria is widely used in design using metallic glasses to account for the asymmetric strengths in tension and compression. The general form of the M-C yielding criterion along the fracture surface is given as,

$$\tau_y = \tau_o - \alpha \sigma_n \tag{1.1}$$

Here, is the effective shear yield stress or critical shear stress, is critical shear failure stress for pure shear fracture, normal stress on the fracture plane, and is an effective friction coefficient or system specific coefficient or material constant or M-C friction parameter, which controls the strength of the normal stress effect. A wide number of significant experimental studies [41-55, Pampillo 1975, Argon 1979, Spaepen 1977] in the area of deformation and fracture behavior of MGs have been reported and shear band/fracture angles in uniaxial or multi-axial state of stress were investigated to predict the plastic yield behavior and M-C friction coefficient parameter for different MGs. They have been independently concluded that yield is not solely controlled by the maximum shear stress. In general, the plastic deformation of MGs is localized in the narrow shear bands, followed by the rapid propagation of these shear bands and sudden fracture. The yield criterion of MGs has been provided in a number of studies [50, 55, Lund and Schuh, 2003 and 2004] through careful measurement of the angles of shear in tension and compression, which are directly related to the coefficient as

$$\alpha = \frac{\cos 2\theta_C}{\sin 2\theta_C} = -\frac{\cos 2\theta_T}{\sin 2\theta_T}$$
(1.2)

Donovan [45] studied a Pd40Ni40P20 based glass in tension, compression, and pure shear and reported a compression/tension strength differential is 23%. Liu et al. [6] studied mechanical properties of two Zr-based bulk amorphous alloys by both tensile and compressive tests at room temperature and reported that the fracture angle in tension and compression are 53° – 58° and 44° – 46°, respectively. Lowhaphandu et al. [47, 48] have used combined uniaxial-plus-pressure loading to explore the yield and failure of Zr-based MGs. These authors showed a small pressuredependence of the yield stress, again manifested as higher strengths in compressive loading states as compared with states of net tension. Mukai et al. [53] studied the mechanical deformation of Pd40Ni40P20 in compression over a wide range of strain rate at room temperature. They reported the fracture angle in tension and compression are 56° and 42°, respectively and also suggested that the yielding of the material behavior follow the Mohr-Coulomb yield criterion but deviates the classical von Mises yield criterion. Lewandowski et al. [54] questioned on the validation of M-C yield criterion in MG systems and reported that for Zr-based and Hf-based MG alloy, there was little pressure dependency on the observed flow/fracture stress during quasi-static compression tests with superimposed pressure.

Thus, it can be clearly observed that due to the practical discrepancies and limitations in experimentation, the fundamental physics behind the yield process could not be understood. Hence the need for computational study at the atomic level was deemed necessary.

Investigator	Material	Tension	Compression
		<i>θ</i> _T (°)	<i>θ</i> _C (°)
Megusar et al. (1979)	Pd80Si20	48-50	
Takayama (1979)	Pd77.5Cu6Si16.5	51	
Donovan (1989)	Pd40Ni40P20		40.7
Liu et al. (1998)	Zr55Ni5Cu30Al10	53-58	
Lowhaphandu et al.	Zr62Ti10Ni10Cu14.5Be3.5	57	41.6
He et al. (2001)	Zr52.5Ni14.6Al10Cu17.9Ti5	55-65	40-45
Inoue et al., (2001)	Cu ₆₀ Hf ₂₅ Ti ₁₅	54	43
Wright et al. (2001)	Zr40Ti14Ni10Cu12Be24	56	42
Mukai et al. (2002)	Pd40Ni40P20	56	42
Lewandowski and Lohaphandu (2002)	Zr _{63.2} Ni _{9.4} Cu _{13.4} Ti _{9.9} Be _{4.1}	50-53	39-42.5
Zhang et al. (2003)	Zr59Ni8Cu20Al10Ti3	54	43
He et al. (2003)	Zr59Cu20Al10Ni8Ti3	54	42.5
Zhang et al. (2004)		56	42
Conner et al. (2004)	La62Al14Cu24Ni24	90	42.5
Sergueeva et al. (2005)		56	42
Ott et al. (2006)	Zr57.4Cu16.4Ni8.2Ta8Al10	54	41
Wu et al. (2006)	Ti62.1Ni2.6Cu4.8Sn8.2Nb22.3	90	45
Wu et al. (2007)	Zr56.2Ti13.8Cu6.9Nb5Ni5.6B	54	40
Yoshikawa et al. (2008)	Zr55Al10Cu30Ni5	53	41
Jiang et al. (2008)	Zr63.2Ni9.4Cu13.4Ti9.9Be4.1	51.6	40.8
	Zr41.2Ti13.8Ni10Cu12.5Be22.	55	44
Baricco et al. (2009)	Cu ₆₀ Zr ₃₀ Ti ₁₀	54	40
Wu et al. (2019)	Ti _{32.8} Zr _{30.2} Ni _{5.3} Cu ₉ Be _{22.7}	54	41.1

Table 1. Shear/fracture angles w.r.t the loading axis for various MGs at room temperature

1.4 Review of computational work on STZ, Failure criteria and strength of metallic glasses

With the advent of molecular dynamics simulation powered by increasingly available computing resources, the results obtained by experimental investigations were verified through computational simulations to get additional fundamental insights. various attempts to model the process of plastic deformation in metallic glasses are summarized in this section. Argon and Kuo [61] studied plastic deformation of amorphous alloy using two-sized bubble raft model and reported two types of deformation units such as diffuse shear transformation and dislocation pair formation.

Kobayashi et al [62] studied a computer simulation work under a periodic boundary condition in order to investigate the atomic mechanism of elastic and plastic deformation of a Cu₅₇Zr₄₃ amorphous alloy, using modified Lennard Jones 4-8 potentials. Srolovitz et al. [63] performed shear deformation of amorphous metal based on free volume model, using computer simulation. They reported a large number of microscopic deformation events observed and discussed the atomic participation in plastic rearrangement. Deng et al. [64, 65] studied the deformation behavior of amorphous materials using MD simulation and discussed how the atoms are participated in the plastic rearrangements. Falk and Langer [66] presented a theory of dynamics STZs for MGs and viscoplastic materials, based on MD simulations.

The results showed a reversible elastic deformation at small applied stresses, an irreversible plastic deformation at larger stresses and a stress threshold above which unbounded plastic flow occurs. Falk [67] studied the MD simulation for ductile and brittle fracture in two-dimensional amorphous solid and reported a small change in interparticle potential leads to a qualitative change in ductility. Lacks [68] studied an inherent structure analysis of viscosity based on results of MD simulations and reported a significant atomic rearrangement in large-scale yielding behavior. Rottler and Robbins [69] studied the yield criterion of an amorphous polymer using MD simulation and reported that the atomic level structures of amorphous polymers and metals are significantly different, but their deformation mechanisms are actually quite similar. The atomistic origin of pressure and normal stress effects on yielding in metallic glasses was studied by Schuh and Lund [70], who used atomistic simulations to examine the deformation characteristics of STZs. Using empirical interatomic potentials, they computed the yield surface of a metallic glasses for biaxial

loading. The yield stress is larger in compression than in tension consistent with the normal stress dependence theory. Fitting their results to Mohr-Coulomb criteria, they identified a friction parameter of $\sigma = 0.12$. in a reasonable agreement with most of the experimental data for metallic glasses. By extending their work to different configurations of STZs with different degrees of dilation. Lund and Schuh proposed that a reasonable range for \propto in a densely packed glasses is 0.12 - 0.4, and suggested that the exact value is determined by factors such as free volume distribution and the chemical and topological short-range interactions.



Fig 1.2: STZ model by Schuh and Lund

1.5 Motivation for the work and objectives

Even though MGs exhibit extreme strength and many other desirable mechanical properties, but other macroscopic deformation properties and mechanisms of yielding and failure are still not thoroughly understood. Shear Bands are particularly important since it play a crucial role in dominating the unique mechanical properties of MGs and in controlling the plasticity and failure of almost all MGs [19-22]. This severely prevents the extensive use or wide potential applications of MGs as advanced structural and functional materials in engineering applications [19, 22 and 23]. Therefore, it is essentially required to fully understand the inherent mechanism of SB behavior such as initiation, propagation, evolution, failure, consequences, and control of SBs in MGs for improving the plasticity and promoting the applications of MGs [19]. There is good amount of works reported in understanding the inherent mechanism behavior [19-22, 24 and 25], propagation [19 and 26], and control [19, 27-30] of SBs in MGs over the last few decades. However, the exact deformation mechanism and the process in MGs are still remains unclear so far, and is an active area of research.

The criteria widely utilized for design using MGs is the Mohr Coulomb criteria of failure. Thus, one important consequence of shear localization in MGs is that the macroscopic plasticyield criterion exhibits a dependence on maximum shear stress as well as hydrostatic pressure or normal stress acting on the shear plane [34]. Table 1 shows typical values of shear band angles in both compression and tension. However, these values show lot of scatter and also have limitations in terms of application of loading conditions. Hence a work probing the physics of deformation at an atomic scale computationally is motivated

Objectives:

- There is a need to understand the atomic basis of failure criteria and yield behavior using simulations based upon state-of-the-art computations based on Density Functional Theory which is an ab initio technique as opposed to empirical inter-atomic potentials utilized in computational work so far.
- This in V estigation aims to pro V ide greater, accurate and reliable insight in qualitati V e and quantitati V e V erification of the underlying mechanisms and understanding of the yielding in this important class of materials.

CHAPTER 2

METHODOLOGY AND PROBLEM DESCRIPTION

2.1 Problem Statement

For the presented work we have worked upon the model presented in Schuh and Lund (2003) paper, replicated their results and later improved the results based on advanced DFT calculations with validation through advanced semi empirical potential available through LAMMPS code. The problem statement and 9 atom model are described ahead.

We have carried out static simulations of the nine-atom STZ model (shown in Fig. 1.2b) with ab initio Kohn Sham DFT method to evaluate the forces on the atoms as opposed to the empirical potential formulations which give the force field. The nine atoms represent a unit of plasticity mimicking the process of shear transformation in which atoms accommodate the shear strain by collectively displacing relative to other atoms. Based on the work of Schuh and Lund [2003] and Lund and Schuh [2004], the initial FCC configuration has been arranged with five atoms in the lower plane and four atoms in the upper plane. The positioning of atoms is explained in the Fig. 2.1 and Fig. 2.2. For a particular configuration of atoms, we evaluate the net force on each atom due to all other atoms. Based on the stress formulation explained we get the stress tensor corresponding to the configuration. Thus, defining the plane of shear and direction of shear we are able to get the normal and stress components. We find the configuration in terms of atomic spacing (r_e) such that the normal stress is zero. Taking configuration with this r_e as the initial configuration we translate the upper plane of atoms with respect to lower atoms as a rigid unit. Thus, the translations are in the plane of normal and shear displacement. We characterize these displacements by discrete positions separated by finite amounts. Finally, when stress components corresponding all the positions are available, we figure out a contour of atomic displacements over which the normal stress is constant. On the points over this contour we calculate the shear stress and plot it against the shear displacement. We compare the plots obtained with the published results of Schuh and Lund [2003] and Lund and Schuh [2004], and noted the max shear value for the corresponding normal stress level. Plotting these max shear stress values against the normal stress values we evaluate the Eq. (1) is strictly followed the Mohr Coulomb criteria and report the slope value as the friction parameter \propto .



Fig 2.1: 9 atom STZ model representation

Lower atoms coordinate

- (1) 0, 0, 0
- (2) $\sqrt{3} r_e, 0, 0$
- (3) $\frac{\sqrt{3}}{2} r_{e}, \frac{r_{e}}{2}, 0$
- $(4) 0, r_e, 0$
- (5) $\sqrt{3} r_e, r_e, 0$

Upper atoms coordinate

 $(6) \ \frac{-1}{3} \frac{\sqrt{3}}{2} r_{e}, \frac{r_{e}}{2}, \frac{\sqrt{6}}{3} r_{e}$ $(7) \ \frac{r_{e}}{\sqrt{3}}, r_{e}, \frac{\sqrt{6}}{3} r_{e}$ $(8) \ \frac{r_{e}}{\sqrt{3}}, 0, \frac{\sqrt{6}}{3} r_{e}$ $(9) \ \frac{5\sqrt{3}}{6} r_{e}, \frac{r_{e}}{2}, \frac{\sqrt{6}}{3} r_{e}$

Fig 2.2: Coordinates in terms of re

2.2 Methodology

> Replicate the published result to understand the procedure

In this first step we wrote a MATLAB code to obtain a qualitative and quantitative match with the results published by Schuh et. al. (2003). The aim was to attain the sinusoidal nature of Shear stress vs shear displacement curve and obtain the friction coefficient value as 0.123 as reported in the paper.

Although the basic procedure for the problem was mentioned in the paper, many subtle details like the inter-atomic spacing for the starting configuration were not reported. Also, the direction of shear of top layer atoms was not explicitly mentioned. Hence in order to understand the methodology of the authors in detail, we tried to simulate the problem with different possible parameters.

With respect to the initial starting structure, we had to figure out the positioning of the atoms and general shape of the STZ utilized by the authors. From the figures in the paper we figured out the positioning of the atoms is as shown in Fig. 2.1. We also initially started our attempts with the common LJ 6-12 potential, however later realized that the author had used the modified LJ 4-8 potential referenced from the paper from Kobayashi et.al. [62]. The formulation of the potential is as follows

	Cu–Cu	Cu–Zr	Zr–Zr
A (eV·Å⁴)	30.7744	71.7076	149.3512
B (eV·Å ⁸)	744.52	2708.56	8313.28
C (eV·Å-1)	-0.03276	-0.04808	-0.07023
D (eV)	0.21095	0.339368	0.531656

 $\phi(r_{ij}) = \frac{A}{r_{ij}^4} + \frac{B}{r_{ij}^8} + Cr_{ij} + D$

Fig 2.3: L-J 4-8 Potential: Formulation and parameters

The direction of shear was initially attempted to be randomly selected within the shear plane passing through the two saddle points in the iso-normal stress surface within the 3D space of possible displacement of top layer atoms within the distance of 1.5 times the inter-atomic spacing between atoms. However later it was understood from the paper from Schuh and Lund [70], that the direction chosen was such that after the shear event the final configuration is mirror image of the first one. That is the top atoms move along the x direction in the Fig. 2.1.

One of the greatest challenges and the determining factor in this exercise was to find the criteria for choosing the inter-atomic spacing for the initial close packed structure. We tried a lot of possible ideas. Initially we started with the value at which the force between two atoms vanishes for the chosen potential. Then we tried the values for which the energy of the system is minimized. But this didn't give proper results as we had constrained the shape of the system to be FCC. Hence energy minimization was obtained at large spacing values. Finally, we reached out the correct procedure by selecting the spacing value as the one which drives the normal stress on the shear plane to be 0. The Fig. 2.5 displays the shear stress vs displacement curve for 0 normal stress level. With these insights we were perfectly able to match the published results qualitatively as well as quantitatively. The value of friction parameter matched exactly. With this we were ready to go ahead with doing these calculations for ab initio setting.



Fig 2.4: Schuh et.al. published results

Fig 2.5: Result from MATLAB code for $\sigma = 0$

Further work with the established method and associated framework

As a next step in the project, we started the runs with DFT-FE code. DFT-FE jobs were executed using the space time super-computing resources. On the completion of the job we get an output file with the net force on each atom. Main task here is to computationally generate the requisite folders containing the input files corresponding to each deformed configuration of atoms. A batch file is used to copy the common files in each folder. Later after each folder has an output file, again a batch file recursively extracts force from the output files and creates an excel file which can be read from the MATLAB code. Once stress tensor for each configuration is evaluated, the further part is exactly similar to the MATLAB code developed for replicating the results. The detail of the code can be found in the code documentation report.

One point to be specifically mentioned is that since DFT-FE runs require much more time than those with empirical potentials, we decided to evaluate the shear stress vs displacement curve only till the first peak is reached i.e. a quarter displacement as compared to that required to get the response in Fig. 2.4 and Fig. 2.5.

Using the mentioned procedure, results were generated for 9 atom Cu-Cu and Zr-Zr system. Based on the results a need was felt to carry out the computations using advanced semi empirical potentials available through LAMMPS and check if there is any deviation from the results obtained from DFT-FE results. After this we made attempt to apply the methodology implemented so far to a relaxed configuration in equilibrium with itself. For this we tried relaxation with a random starting structure and an FCC starting structure. The computational framework here includes computationally generating the input script and respective folders and then submitting them with a batch script. The output file structure is read by MATLAB to pick up the net force on the atoms and corresponding coordinate vectors. So basically, the key step is in all platforms is to get the forces on atoms either pairwise or net sum. The rest of the framework remains same.

CHAPTER 3

THEORETICAL FORMULATION OF STRESS AT DISCRETE ATOMIC LEVEL

3.1 Introduction

Stress being a continuum concept, needs to be applied with a special treatment when it comes to defining it on an atomic level. The macroscopic behavior of solids is widely studied from a microscopic level, using the viewpoints of atomistic mechanics [75]. To bridge the atomistic mechanics and the continuum mechanics, it is important to know the relationships between the microscopic quantities of atoms, and the macroscopic quantities of continua. Atomic-level stress calculation plays a very important role in comparisons of continuum predictions with atomistic simulations, and it allows the intensity and nature of internal interactions in the discrete particle systems to be measured. The atomistic stress can be employed to interpret the results of atomistic simulation in light of continuum mechanical calculations, which have been used in molecular dynamics simulations of solids in a variety of ways, such as characterization of defects, the determination of elastic constants, and the study of the local elastic properties. There are different ways to calculate stress in atomistic simulations. Pioneering work has been done in this field by Born and Huang [72] who used an elastic energy approach to evaluate the stress in lattices by means of the Cauchy-Born hypothesis for homogeneous deformation.

Another widely used stress measure at the atomic scale is the virial stress (*also called the local atomic level stress, system level stress, total stress or pressure tensor*), which is based on a generalization of the virial theorem of Clausius [71] for gas pressure. It is mostly used in molecular dynamical (MD) systems or discrete particle systems and also it gives interpretation of Cauchy stress at atomic level. The quantity includes two parts. The first part depends on the mass and velocity of atomic particles, and the second part depends on interatomic forces and atomic positions, providing a continuum measure for the internal mechanical interactions between particles. The average virial stress [73] over a domain of volume Ω around a particle i at position r_i is given as

$$\sigma^{virial}(r) = \frac{1}{\Omega} \Sigma_i \left[-m_i \dot{u}_i \otimes \dot{u}_i + \frac{1}{2} \Sigma_{j(\neq)i} r_{ij} \otimes f_{ij} \right]$$
(3.1)

Here, i and j are the atomic indices. The summation is over all the atoms occupying the total volume Ω . m_i is the mass of atom i, u_i is the displacement vector of atom i relative to a reference position. The interatomic force f_{ij} applied on atom i by atom j is

$$f_{ij} = \frac{\partial \phi(r_{ij})}{\partial r_{ij}} \frac{r_{ij}}{\parallel r_{ij} \parallel}$$
(3.2)

 \emptyset (r_{ij}) is the pairwise interatomic potential between the atoms. In the above formulation the first term including the momentum flow is neglected for static calculations. Also note that the formulation in equation 3.1 is in terms of pairwise forces between the atoms. However, we get a net force on every atom through DFT calculations. Hence, we see the formulation in terms of net force and atomic position. In the reference book by Tadmor and Miller [75], the expression for Cauchy stress tensor or virial stress is given as

$$\sigma_{ij} = -\frac{1}{\Omega} \Sigma_{\alpha} \left[\frac{P_i^{\alpha} P_j^{\alpha}}{m^{\alpha}} + f_i^{int,\alpha} r_j^{\alpha} \right]$$
(3.3)

f $_i^{int,\alpha}$ represents the ith component of net force on atom α and similarly r^{α} j represents the jth component of the atomic coordinate vector

3.2 Proof of equivalence

Neglecting the momentum flow term provide a proof for equivalence of the equation 3.1 and 3.3 in the previous section

We start out with the central pairwise force based formulation as in Eq. 3.1

$$\sigma = \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} f^{\alpha \beta} \otimes r^{\alpha \beta} = \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} f^{\alpha \beta} \otimes (r^{\beta} - r^{\alpha})$$
$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} [(f^{\alpha \beta} \otimes r^{\beta}) - (f^{\alpha \beta} \otimes r^{\alpha})]$$
$$= -\frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} [(f^{\alpha \beta} \otimes r^{\alpha}) - (f^{\alpha \beta} \otimes r^{\beta})]$$

Here note that summation will not be affected by simply interchanging α and β

$$\sigma = -\frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} [(f^{\alpha \beta} \otimes r^{\alpha}) - (f^{\beta \alpha} \otimes r^{\alpha})]$$
$$= -\frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} [(f^{\alpha \beta} \otimes r^{\alpha}) + (f^{\alpha \beta} \otimes r^{\alpha})]$$
$$= -\frac{1}{\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} [(f^{\alpha \beta} \otimes r^{\alpha})]$$

$$f_i^{int,\alpha}$$
 is the internal force resulting from interactions with other atoms in the system. Now, based
on the principal of interatomic potential invariance [75], the net force on atoms due to internal
particles to the domain is considered the sum of central forces between pairs of particles i.e.

$$f^{int,\alpha} = \Sigma_{\beta(\neq\alpha)} f^{\alpha\beta}$$

Therefore our eq. becomes,

$$\sigma = -rac{1}{\Omega} \Sigma_lpha(f^{int,lpha}\otimes r^lpha)$$

The equivalence between the Eq. 3.1 and Eq. 3.3 is thus prove

3.3 Some additional derivatives and special cases

From the pairwise force formulation for stress we can get the formulation for normal and shear stress components for a particular plane considered. This formulation is useful in the MATLAB code to solve the idealized 9 atom STZ problem using empirical LJ 4-8 potential. This formulation is mentioned in the paper from Schuh and Lund [70] from which the results are compared. Consider φ to be the interatomic potential between the atoms.

The expression for normal stress is given as

$$\sigma_n = \frac{1}{2\Omega} \sum_{i=1}^N \sum_{j=1(\neq i)}^N \frac{\partial \varphi}{\partial r} \frac{(r_{ij}^n)^2}{\|r_{ij}\|}$$
(3.4)

Derivation:

$$\sigma = \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} f^{\alpha \beta} \otimes r^{\alpha \beta}$$
$$\sigma_n = (\sigma \cdot n) \cdot n = \sigma_{ij} n_j n_i$$

n is a unit vector in the normal direction with respect to shearing plane

$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} f_i^{\alpha \beta} r_j^{\alpha \beta} n_i n_j$$
$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} f_i^{\alpha \beta} n_i r_j^{\alpha \beta} n_j$$

Consider the normal component of atomic separation to be $r^{\alpha\beta}$. Here N is the total number of atoms in the system. Also, the central force between atoms can be represented as magnitude of force times the unit vector in the direction of vector connecting the centers of the atoms. Whereas the unit vector is obtained by dividing the vector by its magnitude.

$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} \parallel f_{i}^{\alpha\beta} \parallel \frac{r_{i}^{\alpha\beta}}{\parallel r_{i}^{\alpha\beta} \parallel} n_{i} r_{j}^{n,\alpha\beta}$$
$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} \parallel f_{i}^{\alpha\beta} \parallel \frac{r_{i}^{n,\alpha\beta}}{\parallel r_{i}^{\alpha\beta} \parallel} r_{j}^{n,\alpha\beta}$$
$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} \frac{\partial \varphi^{\alpha\beta}}{\partial r^{\alpha\beta}} \frac{r_{i}^{n,\alpha\beta}}{\parallel r_{i}^{\alpha\beta} \parallel} r_{j}^{n,\alpha\beta}$$
$$\sigma_{n} = \frac{1}{2\Omega} \Sigma_{i=1}^{N} \Sigma_{j=1(\neq i)}^{N} \frac{\partial \varphi}{\partial r} \frac{(r_{ij}^{n})^{2}}{\parallel r_{ij} \parallel}$$

The expression for shear stress is given as

$$\sigma_n = \frac{1}{2\Omega} \sum_{i=1}^N \sum_{j=1(\neq i)}^N \frac{\partial \varphi}{\partial r} \frac{(r_{ij}^n)(r_{ij}^t)}{\|r_{ij}\|}$$
(3.5)

Derivation:

$$\sigma = \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} f^{\alpha \beta} \otimes r^{\alpha \beta}$$
$$\tau = (\sigma \cdot n) \cdot s = \sigma_{ij} n_j s_i$$

n is a unit vector in the normal direction with respect to shearing plane s is a unit vector in the shear direction within the shearing plane

$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} f_i^{\alpha\beta} r_j^{\alpha\beta} s_i n_j$$
$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} f_i^{\alpha\beta} s_i r_j^{\alpha\beta} n_j$$

Consider the normal component of atomic separation to be $r^{n \alpha\beta}$ and the transverse component of the atomic separation to be $r^{t \alpha\beta}$. Here N is the total number of atoms in the system. Also, the central force between atoms can be represented as magnitude of force times the unit vector in the direction of vector connecting the centers of the atoms. Whereas the unit vector is obtained by dividing the vector by its magnitude.

$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} \parallel f_{i}^{\alpha\beta} \parallel \frac{r_{i}^{\alpha\beta}}{\parallel r_{i}^{\alpha\beta} \parallel} s_{i} r_{j}^{n,\alpha\beta}$$
$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} \parallel f_{i}^{\alpha\beta} \parallel \frac{r_{i}^{t,\alpha\beta}}{\parallel r_{i}^{\alpha\beta} \parallel} r_{j}^{n,\alpha\beta}$$
$$= \frac{1}{2\Omega} \Sigma_{\alpha} \Sigma_{\beta \neq \alpha} \frac{\partial \varphi^{\alpha\beta}}{\partial r^{\alpha\beta}} \frac{r_{i}^{t,\alpha\beta}}{\parallel r_{i}^{\alpha\beta} \parallel} r_{j}^{n,\alpha\beta}$$
$$\tau = \frac{1}{2\Omega} \Sigma_{i=1}^{N} \Sigma_{j=1(\neq i)}^{N} \frac{\partial \varphi}{\partial r} \frac{(r_{ij}^{n})(r_{ij}^{t})}{\parallel r_{ij} \parallel}$$

Thus, normal and shear stress components are evaluated for a pairwise force computation.

Now we similarly go ahead to find the expression for normal and shear stress from the stress tensor evaluated from the net force on atoms.

$$\sigma = -\frac{1}{\Omega} \Sigma_{\alpha} (f^{int,\alpha} \otimes r^{\alpha})$$

$$\sigma_{n} = (\sigma \cdot n) \cdot n = \sigma_{ij} n_{j} n_{i}$$

$$\sigma_{n} = -\frac{1}{\Omega} \Sigma_{\alpha} f^{int,\alpha}_{i} r^{\alpha}_{j} n_{i} n_{j}$$

$$\sigma_{n} = -\frac{1}{\Omega} \Sigma_{\alpha} f^{int,\alpha}_{i} n_{i} r^{\alpha}_{j} n_{j}$$

$$\sigma_{n} = -\frac{1}{\Omega} \Sigma_{\alpha} (\mathbf{f}^{int,\alpha} \cdot \mathbf{n}) (\mathbf{r}^{\alpha} \cdot \mathbf{n})$$

$$\tau = (\sigma \cdot n) \cdot s = \sigma_{ij} n_{j} s_{i}$$

$$\tau = -\frac{1}{\Omega} \Sigma_{\alpha} f^{int,\alpha}_{i} r^{\alpha}_{j} n_{j} s_{i}$$

$$\tau = -\frac{1}{\Omega} \Sigma_{\alpha} f^{int,\alpha}_{i} s_{i} r^{\alpha}_{j} n_{j}$$

$$\tau = -\frac{1}{\Omega} \Sigma_{\alpha} (\mathbf{f}^{int,\alpha} \cdot \mathbf{s}) (\mathbf{r}^{\alpha} \cdot \mathbf{n})$$
(3.7)

Now we provide an example of a special case using the Eq. 3.6 and Eq. 3.7 which is used in the codes for the problem described in chapter 2. For this case the z = constant is chosen to be the shear plane and the shearing direction is chosen to be x-axis and the normal direction is chosen to be z-axis. Hence the vector $n = [0 \ 0 \ 1]$ and vector $s = [1 \ 0 \ 0]$ For the above case,

$$egin{aligned} \sigma_{\mathbf{n}} &= -rac{1}{\Omega} \Sigma_{lpha}(\mathbf{f_3^{int,lpha}})(\mathbf{r_3^{lpha}}) \ & au &= -rac{1}{\Omega} \Sigma_{lpha}(\mathbf{f_1^{int,lpha}})(\mathbf{r_3^{lpha}}) \end{aligned}$$

CHAPTER 4

INTROUTION TO DFT FORMULATION AN DFT-FE CODE

4.1 Introductory concepts of Quantum mechanics and DFT

Before diving into the basic formulation of DFT we revisit the concepts in Quantum mechanics and appreciate the need of DFT method. In a nutshell, quantum mechanical system is characterized by Schrodinger's equation, the solution of which is a wave function Ψ , which when multiplied with its complex conjugate gives the probability density function for electrons in the space over which Schrodinger's equation (SE) is solved. Schrodinger's equation is a linear partial differential equation that describes the wave-function or state function of a system. The time independent (no time evolution of the system) form of the SE is as follows:

$$\hat{H}(\Psi) = E\Psi \tag{4.1}$$

The atomic systems which are bounded are governed by this equation. Here H is the Hamiltonian operator which acts on the wave-function. For a non-relativistic particle system, the Hamiltonian operator is

$$\hat{H} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right] \tag{4.2}$$

In the equation 4.2 the first part corresponds to kinetic energy operator for the system and the second part is the potential energy operator for the system. The wave-function Ψ is again in turn a function of coordinates of position of all particles within a system. According to Born Oppenhiemer approximation the nucleus being bulky does not move and thus only electronic positions are considered for atomic systems. The preliminary cases like 1 electron Hydrogen atom have been solved analytically. However, for N atomic system with each atom having M electrons the total variables for Ψ become 3NM for 3 spatial directions. It is analytically impossible to solve the SE for multi-body problems. Hence a simplification through some approximation is necessary

4.1.1 DFT Formulation

The DFT formulation is based upon two fundamental theorems from Kohn and Hohenberg which lay a basis of Kohn Sham DFT formulation

Theorem 1: The external potential is a unique functional of the electron density only. Thus, the Hamiltonian, and hence all ground state properties, are determined solely by the electron density. **Theorem 2:** The ground state energy may be obtained variationally: the density that minimizes the total energy is the exact ground state density

On the basis of the theorem 1, we understand that Hamiltonian is a function of electron density and thus the Kinetic Energy and potential interaction functionals are also in terms of electron density. However, the exact formulation of the interaction functional is something which cannot be determined exactly. This term holds the key to electron-electron and electron-neutron coulombic interaction as well as the exchange and correlation interaction among the electrons. Till date this exchange correlation formulation has not been developed and this is the only approximation used in DFT methodology. Consider the potential due to nuclear interaction as external interaction and denote it by v. Thus H = F+v. F holds the kinetic energy of interacting system of electrons denoted by T and potential due to net electrons and thus formulate $F=T_s+ E_h + E_{xc}$. Here T_s is the KE functional for a non-interacting system, E_h is the coulombic interaction and the Exchange Correlation (E_{xc}) unknown functional is decoupled from the vec functional.

There are well established approximate formulations for the exchange correlation functional such as Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) LDA being the simplest approximate functional is formulated as follows:

$$E_{XC}^{LDA}[n(r)] = \int \epsilon_{xc}(r)n(r)dr$$
(4.3)

However, the LDA ignores the effect due to inhomogeneities in the electron density. The GGA approach overcomes this shortcoming due to its formulation.

$$E_{XC}^{GGA}[n(r)] = \int n(r)\epsilon_{XC}^{hom}[n(r)]F_{XC}[n(r), \nabla n(r)]dr$$
(4.4)

In general, the GGA approximation is much more accurate than the LDA approximation as this formulation includes the effect of gradient of the electron density

4.2 Solution of DFT equation and introduction to DFT-FE code

The Kohn Sham formulation leaves us with a non-linear eigen value problem. The DFT equation is solved through an iterative solution procedure called Self Consistent Field (SCF) method.

Self-consistent field method



Fig 4.1: SCF Flow chat

The flow chart can be summarized in the following steps:

- 1: Choose a set of basis function w
- 2: Set initial ρ
- 3: Calculate $v_{class} = v_{coul} + v_{ne}$
- 4: Determine vxc
- 5: Build Hamiltonian matrix H
- 6: Solve Kohn Sham equation $H \Psi = (H_{kin}+v_{class}+v_{XC}) \Psi$
- 7: Determine occupation numbers n_i of orbitals Ψ_i
- 8: Calculate $\rho = \sum n_i \Psi_i^* \Psi_i$
- 9: If convergence is not met: go to 3 else Calculate energy E and do postprocessing

4.2.1 DFT-FE Code

Majority of codes attempting to solve the DFT equation employ a plane wave basis set. There are lot of disadvantages and limitations of this strategy including the need for large number of waves for region near the atoms. Also, such a basis set doesn't suite well for amorphous materials lacking periodicity. DFT- FE is based on real space discretization of domain using finite elements with the adaptivity provided by the deal.II library. The choice of FE discretization among other real space discretization for DFT in this work is motivated by some key advantages it offers for electronic structure calculations.

In particular, the FE basis naturally allows for arbitrary boundary conditions, provides good scalability on parallel computing platforms due to locality of the basis, and is amenable to adaptive spatial resolution []. In short, the novelty of the DFT-FE as can be understood from its papers is summarized in three points.

1: Higher order adaptive spectral finite-element basis is used to discretize the real space over the DFT equation.

2: Chebyshev polynomial filtered subspace iteration procedure (ChFSI) is employed to solve the nonlinear Kohn-Sham eigenvalue problem self-consistently. ChFSI in DFT-FE employs Cholesky factorization based orthonormalization, and spectrum splitting based Rayleigh Ritz procedure in conjunction with mixed precision arithmetic

3: Configuration forces approach is used to calculate the ionic forces and periodic cell stresses for geometry optimization.

Note that the Exchange correlation functional, criteria for convergence and parameters for atomic coordinates and FE discretization are all provided through an input file. Upon installation an executable becomes available to the user and this can be used to run the electronic problems. Output file is a long document containing information in accordance to the parameter verbosity mentioned in the input file. In our case the final force per atom after the solution has converged is a key result.

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CHAPTER 5

RESULTS AND DISCUSSION

5.1 validation of published results with MATLAB code

This section describes the results obtained while attempting to replicate the published results as described in the chapter 2. For this exercise the LJ 4-8 modified potential is employed and the parameters are exactly same as those used in the reference.

Results for 9 atom Cu system:

The plot in the figure 2.5 shows a shear stress vs displacement response for the 0 normal stress level. For all the normal stress levels the plots are qualitatively similar i.e. sinusoidal in nature. However, there is a linear variation with the normal stress levels for the peak shear stress value normalized by the maximum shear stress value for 0 normal stress

The contour for the atomic displacement corresponding to zero normal stress is as depicted by the following figure as the boundary of the blue region



Fig 5.1: Contour for zero normal stress

Fig 5.2: Shear stress vs displacement response for multiple normal stress levels

Fig 5.2 depicts the stress vs displacement plot for three normal stress levels. Considering the maximum shear stress for zero normal stress to be T_0 , a tensile and compressive normal stress level is suitably chosen

Similar to Fig 5.2 we take a greater number of points between physically acceptable levels of normal stress to plot the maximum shear stress vs normal stress. These points fall in a linear plot and the slope of this plot gives the friction parameter for the modeled STZ.

Results in fig 5.3, fig 5.4 and fig 5.5 are thus summarized as perfectly matching with the published results of a friction factor of 0.123







Fig 5.4: Plot of normalized shear stress vs normal

stress for Zr- system using LJ 4-8 potential



Fig 5.5: Plot of normalized shear stress vs normal

stress for Cu-Zr system using LJ 4-8 potential parameter

5.2 Results from Runs based on DFT-FE code

For the DFT-FE run again we set up the atoms as in case of the MATLAB validation however we limit the displacement of atoms to a quarter of that corresponding to the total sine curve. With this distance the discretization of 10 points is good enough to interpolate the contour at a particular normal stress level. One more important result is that the value of interatomic spacing is 2.6312A° when LJ 4-8 potential is used and 2.4359A° when DFT-FE is used to get the initial zero normal stress level.

DFT results for Cu-Cu system:

Figure 5.6 shows a shear stress vs displacement plot for the 9 atom Cu system using DFT-FE. The value of friction parameter thus obtained by plotting the maximum shear stress vs normal stress level normalized by maximum shear stress for 0 normal stress level using DFT-FE is 0.078. Figure 5.7 shows the plot of normalized shear stress vs normalized normal stress levels.



displacement for Cu-Cu using DFT

Fig 5.7: Plot of normalized shear stress vs normalized normal stress for Cu-Cu using DFT

Also, on noteworthy observation to be made here is that the linear lines passing through points in compression and tension exhibit different slopes. This trend is seen in the plots in Fig 5.8 and Fig 5.9



Fig 5.8: Slope for compressive normal stress of Cu-Cu Shear transformation process



Fig 5.9: Slope for tensile normal stress of Cu-Cu Shear transformation process

DFT results for Zr-Zr system:

Figure 5.10 depicts the normalized shear stress vs shear displacement curve for 9 Zr atom system. This plot clearly shows formation of two peaks and a dip in the nature of the curve till the point it reaches the peak. Figure 5.11 shows the plot of normalized shear stress vs normalized normal stress levels based on the maximum shear stress values corresponding to the second peak in the plot. Note that the value of friction parameter thus obtained is 0.74



Fig 5.10: Plot of normalized shear stress vs shear displacement for Zr-Zr using DFT



Fig 5.11: Plot of normalized shear stress vs normalize normal stress for Zr-Zr using DFT

5.3 validation of the results based on semi empirical LAMMPS potentials

Since the results from DFT runs showed some variance from that obtained from the empirical potential based force field approach through MATLAB code. The points through MATLAB fell exactly on a linear plot. However, the plot of normalized shear and normal stress plotted using DFT-FE results showed a characteristic nonlinearity. Also, the shear stress vs displacement curve for the Zirconium system showed a dip within the sinusoidal nature.

Indeed, the choice of potential affects forces and atomic stress conditions. The table 2. shows results with a variety of potentials applied for the Cu-Cu system.

Species	Force field	Interatomic spacing	Alpha
		(A ^o)	
Cu	LJ 6-12	2.60889	-0.1693
Cu	LJ 4-8	2.6312	-0.123
Cu	EAM U3	2.40629	-0.06513
Cu	EAM U6	2.413	-0.06586
Cu	DFT-FE	2.4359	-0.078
Cu	MEAM	2.3947	-0.082
Cu	Mishin	2.4222	-0.0892
Cu	Smf7	2.4014	-0.073
Cu	Zhou	2.3878	-0.041

Table 2. Simulation results for various interatomic potential formulations

- > We clearly see that the friction parameter varies with the choice of interatomic potential.
- Apart from the value of the parameter we also saw for the qualitative nature of the Normal stress vs shear stress plot.
- With this the plot for meam potential was the best match for the kind of convex nonlinearity in the curve through DFT results







Fig 5.13 The characteristic convex nonlinearity through LAMMPS simulation

LAMMPS validation results for Zr-Zr system using EAM potential

The EAM potential validated the wavy nature of Zr system with slight undulation enveloping the peaks in the graph.



Fig 5.14 Normalized shear stress vs shear displacement for 0 normal stress using EAM potential



Fig 5.15 Normalized shear stress vs Normalized normal stress for EAM potential in Zr system

CHAPTER 6

CONCLUSION AND SCOPE OF FUTURE WORK

Based on the simulation results obtained studying the process of shear transformation, we can conclude the following:

- In the figure 2.1, the x displacement of atoms from A to C correspond to the sinusoidal response. Hence if the applied shear stress is enough to cause displacement of atoms to point B, then the process of shear transformation is completed.
- The dependency of yield strength over the normal stress is linear for all the empirical, semiempirical or the ab-inito force evaluation. Thus, the Mohr-Coloumb yield criteria is justified at an atomic level.
- In general, both the advanced semi empirical potentials and the DFT force evaluations yielded a smaller value of friction parameter than the empirical potential calculation.
 Zr-Zr: friction parameter 0.074
 Cu-Cu: friction parameter 0.078
- The nature of plots in case of Zr and Cu in the DFT calculations indicate that bond formations and breaking have an impact on the Shear Transformation process. And this process is not modelled effectively by empirical formulations.

The results obtained from the study indicate the following course of future work:

- Study the effect of bonding i.e. electron density during the process of shear transformation. This will help to understand the different yielding behavior for various species as indicated by DFT-FE results
- Model orientation independent larger STZ with more than 50 atoms to accommodate heterogeneity due to multi species. Relaxation technique can be used for the process
- The methodology of computation can be used to model system with multiple components to realistically determine the friction parameter for a stoichiometric metallic glass system.

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Appendix

• Unit Conversion chart for atomic problems used for computation

Pressure:

1 ev/Angstrom³ = 160.21766208 GPa 1 Ha/Bohr³ = 29421.02648438959 GPa 1 GPa = 10 kbar = 145037.738007218 pound/square inch 1 Gbar = 100,000 GPa 1 Mbar = 100 GPa 1 kbar = 0.1 GPa 1 atm = 1.01325 bar = 0.000101325 GPa 1 pascal = 1.0E-09 GPa 1 TPa = 1000 GPa = 10 Mbar

Force:

1 Ry/Bohr = 25.71104309541616 ev/Angstrom 1 Ha/Bohr = 51.42208619083232 ev/Angstrom

Energy:

1 Hartree = 2 Ryd = 27.211396 ev (nist - 27.21138386) 1 kJ/mol = 0.0103642688 ev/atom 1 Joule = 6.24150965x10¹⁸ ev (CODATA)

 $1 \text{ ev} = 1.6021766208 \times 10^{-19} \text{ Joules}$

Length:

1 Bohr = 0.529177208 Angstrom