Simulations of Mechanical Properties of CuZr and CuMg Metallic Glasses

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Preface

This thesis is submitted in candidacy for the Ph.D. degree from the Technical University of Denmark (DTU). It is based on the work carried out at the Center for Atomic-scale Materials Design (CAMd), Department of Physics at DTU from February 2005 to February 2008 under the supervision of Professor Karsten W. Jacobsen and Professor Jacob Schøtz. Financial support was provided by the EU Network on bulk metallic glass composites (MRTN-CT-2003-504692 “Ductile BMG Composites”), Copenhagen Graduate School for Nanoscience and Nanotechnology (CONT) and DTU.

I am grateful to my advisers Karsten Wedel Jacobsen and Jakob Schiøtz for competent guidance throughout the years and whose patience and inspiring discussions made this work possible. I thank Ole Holm Nielsen, Jens Jørgen Mortensen and Marcin Dulak for help and patience in solving many technical problems.

I thank Sergey Dobrin, Eva Fernandez, Niels Jensen, Jose Martinez, Duncan Mowbray, and Mikkel Strange for proof reading this thesis and moral support. I also give many thanks to Duncan Mowbray for both his help with figures in this thesis and our many useful discussions. Thanks to my office colleagues and to all CAMd/CINF employees for creating a great social environment.

I especially owe thanks to my family, for loving support and understanding in letting me follow my dreams. They taught me the value of self-responsibility and hard work.
Abstract

Molecular dynamic simulations have been performed to study the mechanical properties of Cu$_{15}$Mg$_{85}$, respectively and Cu$_{50}$Zr$_{50}$ metallic glasses.

The many body interaction between atoms are described at the Effective Medium Theory interatomic potential level of theory. In order to treat Cu$_{50}$Zr$_{50}$ a new interatomic potential has been constructed. The interatomic potential was fitted to lattice constants, elastic constants and cohesive energies of Cu, Zr and Cu$_{50}$Zr$_{50}$ in the B2 structure.

We tested the optimized Cu$_{50}$Zr$_{50}$ interatomic potential by comparing the lattice properties of several CuZr structures to accurate Density Functional Theory calculations and find a satisfactory agreement. Furthermore, with the CuZr interatomic potential we are able to describe the thermodynamics of CuZr glass during cooling in good agreement with experiments.

Two different method have been used to study the formation of shear bands during plastic deformation: i) a simple shear deformation, and ii) nanoindentation with a cylindrical indenter. For the simple shear deformation we observe formation of shear bands with a width of 5 nm and 8 nm for Cu$_{50}$Zr$_{50}$ and Cu$_{15}$Mg$_{85}$, respectively.

The formation of shear bands during nanoindentation was found to be dependent on the indentation velocity, radius of the indenter and the cooling rate. Shear bands formation is more clear when we use low velocity of nanoindentation, larger radius of the indenter and when the samples are cooled slowly.
Resumé

De mekaniske egenskaber af Cu$_{15}$Mg$_{85}$ og Cu$_{50}$Zr$_{50}$ metalliske glasser er blevet undersøgt ved hjælp af molekyldynamik.

Vekselvirkningerne mellem atomerne er beskrevet med et Effective Medium Theory potential, der medtager mangelegeme-effekter i vekselvirkningerne. Det interatomare potential blev tilpasset til gitterkonstanter, elastiske konstanter og kohesivenergier for Cu, Zr og Cu$_{50}$Zr$_{50}$ i B2 strukturen.

Vi afprøvede det optimerede potential for CuZr ved at sammenligne krystatlegenskaber for et antal CuZr strukturer med mere nøjagtige beregninger baseret på pathedsfunktionalteori, og finder tilfredsstillende overensstemmelse. Potentialet er desuden i stand til at beskrive termodynamikken af en CuZr glas under afkøling fra vskefasen med god overensstemmelse med eksperimentelle data.

To forskellige metoder blev brugt til at undersøge dannelsen af forskydningbånd (shear bands) under plastisk deformation: dels simpel deformation under en forskydning, dels nanoindentation, som simulerer en hårdhedsprøvning med cylindriske prøvelegeme. Ved den simple forskydningsdeformation observeres dannelse af forskydningbånd med bredder på 5 og 8 nm i henholdsvis Cu$_{50}$Zr$_{50}$ og Cu$_{15}$Mg$_{85}$.

Vi observerede, at dannelsen af forskydningsbånd ved nanoindentation afhænger af indentationshastigheden, prøvelegemets diameter og den hastighed, hvormed glassen blev afkolet under sin dannelse. Dannelsen af forskydningsbånd er klarest ved lave hastigheder, store prøvelegemer og langsomt afkølede metalglasser.
List of Included Papers

Paper I:

An Interatomic Potential for Studying CuZr Bulk Metallic Glasses

Anca Păduraru, Abdel Kenoufi, Nicholas P. Bailey and Jacob Schiøtz


Paper II:

Computer simulations of nanoindentation in Mg-Cu and Cu-Zr metallic glasses

Anca Păduraru, Nicholas P. Bailey, Karsten W. Jacobsen, and Jacob Schiøtz

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Chapter 1

Introduction

The purpose of this thesis is to study the mechanical properties of metallic glasses through atomistic simulation. A glass is a solid material obtained from a liquid which does not crystallize during cooling. Most metals do crystallize as they cool, with the atoms arranged in a regular spatial pattern called a crystal lattice. A metallic glass (metallic amorphous) is obtained if the liquid is cooled fast enough to avoid crystallization. If this happens, the atoms are packed into a random manner similar to that in the liquid state, lacking the long range order characteristic at crystalline materials. Due to the lack of long range order, the plastic deformation is completely different from that in the conventional materials. While in crystals the plastic deformation is carried by dislocations, metallic glasses plastic deformation is correlated with localized deformation events such as shear bands. This is believed to be the reason why these materials have remarkable mechanical properties [1, 2] such as high strength, fracture resistance, elastic limit and yield stress (about $0.02Y$, where $Y$ is Young’s modulus) and corrosion resistance. Some metallic glasses are ductile at room temperature, however, most are brittle. To improve the ductility of these materials a better understanding of their structure and plastic deformation is required.

We performed atomistic simulations on $\text{Cu}_{15}\text{Mg}_{85}$ and $\text{Cu}_{50}\text{Zr}_{50}$ metallic glasses in order to study the mechanical properties by performing shear deformations and nanoindentation. We use the Effective Medium Theory (EMT)
interatomic potential to describe the interactions between the atoms.

1.1 Outline of this thesis

An introduction to EMT and the simulation methods are presented in chapter 3. In the same chapter, a summary of other methods (particularly other potentials) used to perform simulations on glasses is included together with justification for our choice of potential. Chapter 4 presents the potential we fitted for modeling the mechanical properties of CuZr metallic glasses. Chapter 5 describes the shear deformation, which is the method we use to measure the width of the shear bands for CuZr and CuMg metallic glasses. Finally, chapter 6 contains a study of shear band formation and how this can be influenced by different parameters during simulated nanoindentation. General conclusions follow in chapter 7.
Chapter 2

Metallic Glasses

A glass or an amorphous material is a disordered solid which does not possess the long range periodicity present in a typical crystal. The definition of a glass is made only based on its disordered structure, regardless of its chemical composition. Glass formation involves a cooling mechanism different from crystalline materials. A glass is obtained by rapid cooling from the liquid and is formed when the liquid becomes increasingly viscous during cooling and fails to crystallize. An important characteristic of glass formation is the glass transition temperature, which we will discuss in this chapter. We will also present some experimental methods for making glasses, the mechanical properties and their applications. Finally, we will provide an overview of what can be done using computer simulations and why they are useful.

2.1 Glass transition temperature

The glass transition temperature is a characteristic of nanocrystalline materials, which can be either organic polymers, metallic glasses or other inorganic glasses. During cooling of a material, as the temperature decreases, the specific volume of the liquid decreases.

The slope of the volume versus temperature curve, normalized to the sample volume as shown in Fig. 2.1(a), is called the bulk thermal expansion
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Figure 2.1: Specific volume as a function of temperature for a series of materials. (a) The liquid-to-crystalline solid transformation. A discontinuous change in volume occurs at the melting temperature $T_m$. (b) The liquid-to-glass transformation (the liquid-to-crystal curve shown as reference). The temperature at which the slope of the liquid-glass curve changes is the glass transition temperature $T_g$ reproduced from Schaffer et. all \[3\].

The coefficient $\alpha_v$,

$$\alpha_v = \frac{1}{V} \frac{dV}{dT}.$$  \hspace{1cm} (2.1)

When the cooling rate is not sufficiently high, a sample can crystallize at a temperature $T_m$ called the melting point. In this case, at $T_m$ we can observe a sudden drop in the volume versus temperature curves shown in Fig. 2.1(b). This drop is a consequence of the change in structure, from that of a liquid to that of a crystalline solid. Below $T_m$ the specific volume continues to decrease linearly with temperature. A crystal is the lowest energy state, and therefore the most stable state for a material at low temperature. In some materials, it is possible to avoid crystallization by cooling the liquid at a high rate, so that the diffusion necessary to establish long range order is suppressed. In this case, the volume of the sample decrease with the same slope as for the liquid before the melting temperature, as shown in Fig. 2.1(b), forming a supercooled liquid. The slope of the curve for supercooled liquids decreases at a certain temperature $T_g$ below that of the crystal melting temperature $T_m$, since a supercooled liquid cannot have a smaller volume than a crystal. The slope of the enthalpy versus temperature curve changes as well at the
same temperature $T_g$. The temperature at which the slope of this curves changes is called the glass transition temperature $T_g$.  

2.2 Properties and applications

Mechanical properties of metallic glasses are different from those of conventional materials. Due to lack of long range order, plastic deformations cannot be carried out by lattice defects, as would happen in a crystal. In the absence of a crystal slip plane, the plastic flow is concentrated into shear bands, thus leading to high flow stresses [4]. One of the first interpretations of glass deformation was made by Argon [5]. They found that the deformation mechanism appears to be of a very local nature. This localized strain is produced by repeated nucleations (tiny regions of agglomeration) of shear, which are confined within regions of free volume. According to Falk and Langer [6], plasticity involves shear transformation zones, which operate as centers of localized deformation. These models are supported by simulations of deformation in metallic glasses [7, 8] and observations of localized events [9, 10, 11].

For the purpose of developing reliable structural bulk metallic glasses, several attempts have been made to enhance ductility [13]. A ductile material is capable of undergoing large plastic deformations before fracture, and those that fracture with little accompanying plastic deformation are brittle. To enhance ductility, some composite materials have been synthesized by inducing a second crystalline phase to generate multiple shear bands and to avoid and/or delay the propagation of the shear bands through all the sample. The ductility of glasses can also be enhanced by small changes in composition. Das et al. [12] showed (Fig. 2.2) that the presence of nanocrystals in Cu$_{50}$Zr$_{50}$ enhances ductility, but not so efficiently as does the addition of 5% Al in the composition of the glass.

Due to their structure, metallic glasses are materials with special mechanical properties. These include high strength, high strain limit for the Hookean elasticity, fatigue resistance, and often corrosion resistance. The fracture
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Figure 2.2: Stress-strain curves of (a) Cu$_{50}$Zr$_{50}$ and (b) Cu$_{47.5}$Zr$_{47.5}$Al$_5$ under the compression test at a strain rate of $8^{-4}\text{s}^{-1}$, showing a highly "work-hardenable" metallic glasses up to 18 % strain. The inset shows the true stress-strain curve of alloy (b) Cu$_{47.5}$Zr$_{47.5}$Al$_5$ as reproduced from Das et. al [12].

Toughness in metallic glasses is higher than in conventional glasses. In Fig. 2.3 we see that the toughest metallic glasses lie amongst the best of metals [14].

The tensile fracture strength $\sigma_f$ and the hardness $H_v$ of metallic glasses have a tendency to increase with the Young’s modulus, $E$, of these materials. Fig. 2.4 shows the relationship between $\sigma_f$, $H_v$ and $E$ for bulk amorphous and conventional crystalline alloys. The amorphous alloys have both a high $\sigma_f$ of 840-2100 MPa and a high $E$ of 47-102 GPa [2].

We will now consider potential applications of metallic glasses as structural materials and provide some examples of applications which are related to the material’s properties. The high hardness of metallic glasses may be used for tooling, particularly as knife edges. The wear resistance combined with corrosion resistance of metallic glasses is used in coatings for industrial equipment, machinery and valves, in high wear, extreme temperature and high corrosion environments. Metallic glass alloys are also used in the electronic casings in-
CHAPTER 2. METALLIC GLASSES

Figure 2.3: Fracture toughness and Young’s modulus for metals, alloys, ceramics, glasses, polymers and metallic glasses (the gray circles represents metallic glasses). The contours show the toughness $G_c$, reproduced from Ashby and Greer [14].

Industry and for hinge applications, see Fig. 2.5. Here they have the advantage that they enable smaller, thinner and more durable designs [15].

Excellent wear resistance and high strength to weight ratio compared to titanium and/or stainless steel make these materials good candidates for medical devices. These include reconstructive devices, fractured fixations, spinal implants, and instrumentation [15]. For medical instrumentation, they can yield surgical blades that are sharper than steel and less expensive than diamond, see Fig. 2.6. Metallic glasses are also used in the production of sporting goods and leisure products such as golf clubs, tennis rackets and baseball bats amongst others. High polish-ability, abrasion resistance and corrosion resistance [14] make them good candidates for producing jewelry such as rings, watches cases, and pens, see Fig. 2.7.
Figure 2.4: Relationship between the tensile fracture strength $\sigma_f$ or the Vickers hardness $H_v$ and Young’s modulus $E$ for bulk amorphous and conventional crystalline alloys, reproduced from Inoue [2].

2.3 Processing of metallic glasses: Experimental methods

A glass is formed if a liquid is cooled sufficiently fast to avoid crystallization. The most important processing step in producing metallic glasses is the quench from the liquid state. The quench rate must be very fast ($\geq 10^6$ K/s) to “freeze” the atoms in the metastable structure. Therefore, rapid heat removal from the bulk is needed during cooling.

The gun technique developed by Duwez [16] was one of the earliest rapid solidification method used to produce amorphous alloys. In the gun technique, a molten alloy is ejected by using a shock wave to generate very small ($\sim 1\mu m$) droplets impacting at sonic velocity onto a chilled substrate, as shown in Fig. 2.8.

The most often used technique for production of metallic glasses is melt spinning, which is used to obtain wires and ribbons. This method has the advantage of obtaining the metallic glass products in a continuous form with
cooling rates of the order of $10^5$-$10^6$ K/s. Metallic ribbons are obtained with this method by allowing a stream of the molten alloy to flow onto a rapidly moving substrate. The principle of the method is shown in Fig. 2.9. By ejecting a jet of molten alloy into a stream of water a wire of metallic glass can be obtained, as shown in Fig. 2.9.

In the methods described above, the cooling rates achieved is of the order of $10^6$ K/s. A much higher cooling rate may be achieved using pulsed laser quenching. In this method a very thin ($\sim 100$ nm) surface layer is melted by an incident beam of duration as short as a few picoseconds. The layer on top of a large cold substrate may experience ultra rapid cooling, as fast as $10^{14}$ K/s [1].

Melt atomization is an important technology for producing rapidly solidified
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Figure 2.6: Applications of metallic glasses as medical devices for (a) the orthopedic field due to excellent wear resistance, biocompatibility and high strength to weight ratio and (b) surgical blades with lower edge degradation and improved sharpness over steel. Reproduced from [15].

powders. Atomization is a process whereby powder particles are formed from the quenching and solidification of discrete droplets of liquid metal.

Figure 2.7: Applications of metallic glasses for (a) watches cases, (b) pens and (c) jewelry (rings) due to polish-ability and abrasion and corrosion resistance. Reproduced from [15].
2.4 Measuring hardness with indentation

An indentation test is an excellent way to measure the mechanical properties of very small volumes of materials. In an indentation test, a hard tip, typically a diamond, is pressed into the sample with a known load. After some time, the load is removed. The area of the residual indentation in the sample is measured and the hardness, H, is defined as the maximum load, P, divided by the residual indentation area.

Hardness is a measure of a material’s resistance to plastic deformation during
Figure 2.9: Principal methods of rapid quenching from the melt: (a) drop smasher, using levitation-melting by induction, the pistons are pneumatically accelerated and come into action when the falling drop breaks a light beam, (b) melt-spinning, (c) pendant drop melt-extraction and (d) twin-roller quenching device.

nanoindentation. A material’s resistance of the materials to indentation is not necessarily the same as its resistance to abrasion. However, a hardness measurement obtained from an indentation test can be used as an empirical test for abrasion resistance. In general, materials which possess a high hardness also have a high resistance to abrasion.

There are various types of indentation tests available [3, [18, [19], the most common being the Brinell test, the Vickers diamond test and the Rockwell test.

**Brinell Hardness Test** is one of the oldest hardness test methods in com-
mon use today. The Brinell test is frequently used to determine the hardness of steels and cast irons. By varying the test force and ball size, nearly all metals can be tested using a Brinell test. In its original form, a Brinell test uses a steel ball indenter of 10 mm diameter forced into the sample by a controlled test force. The force is maintained for a specific time, normally 10 - 15 seconds. After this, the indenter is removed leaving a round indent in the sample. The size of the indent is determined optically by measuring two diagonals of the round indent using either a portable microscope or one that is integrated into the load application device. The Brinell hardness number is the ratio of the test force to the surface area of the curved indent. The indentation is considered to be spherical with a radius equal to half the diameter of the ball. The average of the two diagonals is used in the following formula to calculate the Brinell hardness:

$$H_B = \frac{\text{applied load (kg)}}{\text{surface area of the impression (mm}^2\text{)}} = \frac{2F}{\pi D (D - \sqrt{D^2 - d^2})} \quad (2.2)$$

where $D$ is the diameter of the indenter, $d$ is the diameter of the impression and $F$ is the load as shown in Fig. 2.10.

![Figure 2.10: Brinell hardness test](image)

However, the Brinell test is not suitable for testing very hard materials. This is because as the hardness of the material approaches that of the indenter, there will be a tendency for the indenter to deform.

The Vickers Test (HV) was developed in England in 1925 and was formally known as the Diamond Pyramid Hardness (DPH) test. The Vickers test has
two distinct force ranges, micro (10 g to 1000 g) and macro (1 kg to 100 kg), to cover all testing requirements. All Vickers tests use the same 136° pyramidal diamond type indenter, which forms a square indent. As in the Brinell test, the indenter is pressed into the sample by an accurately controlled test force for 10-15 s. After removing the indenter, the size of the indent is determined optically by measuring the two diagonals of the square indent. The Vickers hardness number is the ratio of the test force to the surface area of the indent. The average of the two diagonals is used in the following formula to calculate the Vickers hardness:

\[ H_D = \frac{\text{applied load (kg)}}{\text{surface area of the impression(\(mm^2\))}} = \frac{\text{Constant x test force}}{\text{indent diagonal squared}} = \frac{\sin \theta/2F}{D^2}, \]  

(2.3)

where \( \theta = 136^\circ \), \( F \) is the applied force in kg and \( D \) is the mean diagonal length in mm as shown in Fig. 2.11.

Figure 2.11: Vickers hardness test [19].

The Rockwell Hardness test also uses a machine to apply a specific load and then measure the depth of the resulting impression. The indenter may either be a steel ball of some specified diameter or a spherical diamond-tipped cone at a 120° angle with a 0.2 mm tip radius, called a braille. A minor load
of 10 kg is first applied, which causes a small initial penetration to seat the indenter and remove the effects of any surface irregularities. The dial is then set to zero and a larger load called the major load, is applied. Upon removal of the major load, the depth reading is taken while the minor load is still on. The hardness number may then be read directly from the scale. The indenter and the test load determine which hardness scale that is used (A, B, C, etc).

While lowering the indenter into the sample a load displacement curve is recorded. The load displacement curve provides information about the macroscopic deformation character of the material [20].
Chapter 3

Theoretical and Computational Methods

This chapter contains details about the theory and molecular dynamics methods used to perform simulations of metallic glasses. In order to study into the mechanical properties of metallic glasses, we need large systems (on the order of up to 1 million atoms). This makes impractical the use of quantum theories and \textit{ab initio} methods, which, although accurate are very time consuming, and may only simulate systems of up to about 200 atoms. To address this problem, we will use Effective Medium Theory (EMT) \cite{21, 22, 23, 24}, which is explained in section 2.1. EMT uses a potential which is derived from Density Functional theory (DFT), and allows extensive molecular dynamics simulations to be performed. The parameters of the interatomic potential given by EMT will also be discussed. Sections 2.2 and 2.3 contain information about how we perform the Molecular Dynamics (MD), how we integrate the equation of motion, how we minimize the energy without using the temperature, and finally how we perform MD at different temperatures.
3.1 Methods for simulating metallic glasses

One of the most common ways to simulate large systems is using a Lennard Jones (LJ) potential, which is given by the expression:

\[ \Phi_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]. \] (3.1)

for the interaction potential between a pair of atoms.

The potential has an attractive tail at large distances \( r_{ij} \), but reaches a minimum and becomes strongly repulsive at shorter distances.

This potential has been used to simulate glassy systems as \( \text{Fe}_{83}\text{M}_{17} \) (M: C, B, P), CuY, ZrTi and model glasses [25, 26, 27, 28, 6]. Evtteev et al. [25] use this potential to describe the interaction of atoms in \( \text{Fe}_{83}\text{M}_{17} \) (M: C, B, P) metallic glasses and to study the individual characteristics of local atomic ordering on structure formation. Molecular dynamics has been performed to produce the glasses in the compositions mentioned above, and radial distribution functions were calculated as shown in Fig. 3.1. The results they obtain are in good agreement with experiments.

The same study was made of CuY glasses [26]. However, in this case they found poor agreement with experiments in the case of \( g_{\text{CuCu}}(r) \), as is shown in Fig. 3.2. The reason why the position and amplitude of the first peak for the pair distribution functions \( g_{\text{YY}} \) and \( g_{\text{CuY}} \) is in good agreement could be because they were heavily weighted in the fitting procedure.

The Lennard Jones potential was also used to describe interactions in a model glass and to simulate nanoindentation in order to study the shear bending and strain localization under the indenter [28, 6].

Lennard Jones potential describes some systems well, and is useful for investigations where the focus is fundamental issues, rather than studying the properties of a specific material. However, such pair potentials cannot describe correctly the transition metals, particularly the bulk properties of metals, e.g. elastic behavior. It is also not possible to describe atoms with different coordination numbers using the same pair potential.
Figure 3.1: Pair distribution function of the amorphous alloys: Fe$_{83}$C$_7$ (1), Fe$_{83}$B$_7$ (2) and Fe$_{83}$P$_7$ (3). Models are shown by a solid line and dots represent X-ray pair distribution functions from experimental data for (2) and (3) alloys, reproduced from Ecteev et al. [25].

In the literature it has been proposed that other methods may serve as alternatives to the Lennard Jones potential. One is the Embedded-Atoms Method (EAM) potential [29] used, for example, to study glasses such as CuW and CuAg [30, 31]. Based on this method, molecular dynamics has been applied to obtain an atomic description of the glass formation process in a eutectic C$_{40}$Ag$_{60}$ alloy [31]. In this case, structure and glass forming ability were studied. Their results showed that EAM correctly predicts the glass transition. Also, the structure analysis through the calculated radial distribution function revealed the formation of different clusters at different quenching rates during the quenching process as shown in Fig. 3.3.
A similar method to EAM is the Effective Medium Theory interatomic potential, which has proved to be a good method to describe the properties of close packed metallic alloys \cite{21, 22, 24}. This method was used by N. Bailey \cite{32} to describe both glass formation ability and structural properties in CuMg glassy alloy. This method was also efficient in studying the mechanical properties of CuMg glasses and the shear band deformation mechanism \cite{33, 34}. In order to study the shear bending, a simulated uniaxial tension test was performed \cite{34}. This showed that a necking instability occurred rather than shear bending, as shown in Fig. 3.4. For initiating the shear bands a notch was used. In the same uniaxial test using a notch it was shown that the deformations then takes place in shear bands that lead away from the notch at 45°, as shown in Fig. 3.5.

Using the EMT interatomic potential, we performed simulations in order to study the mechanical properties of CuZr metallic glasses, as discussed
Figure 3.3: Two dimensional cross-sectional projections of the structures obtained at different quenching rates for a Cu$_{40}$Ag$_{60}$. (a) 1x10$^{11}$, (b) 1x10$^{13}$, (c) 1x10$^{14}$. These projections exhibit the structure of CuAg alloys. The transparent circles represent the Ag atoms and the colored circles represent the Cu atoms. The retention of amorphous structure requires an extremely high cooling rate (1x10$^{14}$ K/s) as reproduced from L. Qi et al. [31].

in Paper I. Thermodynamic properties were recorded during cooling of the system and the glass transition, temperature and structure study results were compared with experiments. In order to study the mechanical properties, we have performed shear and nanoindentation tests. Details of these simulations will be presented in the following chapters.

CuZr glass formation and structure have been simulated before by Duan et al. [35]. They fitted the effective Rosato-Guillope-Legrant-type force field parameters to data, such as lattice constants, cohesive energies and bulk moduli obtained using a quantum mechanical model. They performed molecular dynamics to obtain the glassy system, and observed a change in
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Figure 3.4: Outline of a $14 \text{ nm} \times 14 \text{ nm} \times 14 \text{ nm}$ MgCu metallic glass deformed by uniaxial tension after 0%, 20%, 40%, 60%, 80% and 100% strain [34].

Figure 3.5: Visualization by stripe painting in a $56 \text{ nm} \times 56 \text{ nm} \times 18 \text{ nm}$ MgCu metallic glass deformed at different amounts of strain [34].

the slope of the volume versus temperature curve that corresponds to the glass transition, as shown in Fig. 3.6. Near the glass transition temperature they observed a change in slope of the variation of volume, enthalpy and entropy with temperature. They calculated the radial distribution functions and the coordination number, shown in Fig. 3.7.

The results we obtain performing simulations with a fitted EMT interatomic potential for these properties are slightly better, and these results are discussed in chapter 3.

Similar methods have been used to describe the interactions of very large metallic glass systems. These include quantum Sutton-Chen many-body potentials for studying CuAg and CuNi glasses [38], the Finnis-Sinclair type pair functional potential for ZrNi [39], and the same ZrNi metallic glass
Figure 3.6: Volume versus temperature curves for Cu_{46}Zr_{54} obtained for three different quenching rates. The glass transition temperature is where the slope of the curve changes between 600K and 800K. Reproduced from [35].

| & \( N \text{ (Cu-Cu)} \) & \( N \text{ (Cu-Zr)} \) & \( N \text{ (Zr-Cu)} \) & \( N \text{ (Zr-Zr)} \) \\
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<td>5.6</td>
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<tr>
<td>Cu_{46}Zr_{54} (EXAFS)(^b)</td>
<td>6.0</td>
<td>5.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu_{46}Zr_{54}(^c)</td>
<td>3.2</td>
<td>7.6</td>
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Figure 3.7: The numbers of nearest neighbor correlations obtained from different techniques [35]. \(^a\)Reference [36], \(^b\)Reference [37], \(^c\)Reference [35]. The experimental data was chosen by Duan et al. to compare with their simulation data.

systems adapted to Hausleitne-Hafner interatomic potentials [40] analyzed within the mode coupling theory (MCT) [41].

### 3.2 Introduction to Effective Medium Theory

The energy of an atom in an arbitrary environment is calculated within EMT in order to calculate the interatomic forces. The energy of an atom in the working environment is calculated first in a reference system. In our case, the
reference system is a perfect crystal. The reference system and the actual system are related through the lattice constant, which is adjusted in such a way that an atom in the fcc crystal is surrounded by the same average electron density as an atom in the real system.

The total energy of the \( i \)th atom, after taking into account the previous assumptions, will be the sum of two terms. These are the cohesive energy \( E_{c,i} \), which is the energy of the reference system, and a correction \( E_{AS,i} \), called the atomic sphere correction, which estimates the difference in energy between the two systems. The total energy of the system, \( E \), is then:

\[
E = \sum_i [E_{c,i}(n_i) + \Delta E_{AS,i}].
\]

The atomic sphere correction is calculated as the difference between a pair potential for the \( i \)th and \( j \)th atoms, \( V_{ij} \), in the actual system and the pair potential in the reference system, \( V_{ij}^{ref} \). The one electron correction is included in the atomic sphere correction by adjusting the pair potentials, so that we obtain

\[
E = \sum_i \left\{ E_{c,i} + \frac{1}{2} \left[ \sum_{j \neq i} V_{ij}(r_{ij}) - \sum_{j \neq i} V_{ij}^{ref}(r_{ij}^{ref}) \right] \right\},
\]

where \( r_{ij} \) and \( r_{ij}^{ref} \) are the distances between the \( i \)th and \( j \)th atoms in the working and reference systems, respectively.

We will begin by considering a mono-atomic system. Before we may calculate the total energy, we must first evaluate the density. We may then express the density \( n_i \) of an atom \( i \) as:

\[
n_i = \sum_{j \neq i} \Delta n_j(s_i,r_{ij}).
\]

We assume that the density contribution to an atom \( i \) from a neighboring atom \( \Delta n_j(s,r) \) at a distance \( r \) averaged over a neutral sphere of radius \( s \) has the form:

\[
\Delta n(s,r) = \Delta n_0 e^{(s-s_0) - (r-\beta s_0)},
\]
where $s_0$ is the equilibrium neutral sphere radius, and $\eta_1$ and $\eta_2$ describe the exponential decay of the density. Here,

$$\beta = \sqrt{2} \left( \frac{16\pi}{3} \right)^{\frac{1}{3}} \quad (3.6)$$

is a geometric factor given by the assumption that the reference system is an fcc crystal, and only the 12 nearest neighbor contributions are taken into account. The nearest neighbor distance is taken to be $d = \beta s_0$. As mentioned before, the two systems are linked by adjusting the lattice constant through the neutral sphere radius, $s$, to find a relation between $s$ and the density, $n$. From DFT calculations, we find that the relation between the neutral sphere radius and the density is also an exponential, so that

$$n(s) = n_0 e^{-\eta(s-s_0)}. \quad (3.7)$$

Since the reference system is an fcc crystal, we have $\frac{\Delta n}{n_0} = 12$, $r_{fcc} = \beta s$ and the exponential decay factors are related by $\beta \eta_2 = \eta + \eta_1$. Solving equation (3.7) using equation (3.5), we find the neutral sphere radius of the $i$th atom is:

$$s_i = s_0 - \frac{1}{\beta \eta_2} \log \left( \frac{\sigma_1,i}{12} \right), \quad (3.8)$$

where $\sigma_{1,i}$:

$$\sigma_{1,i} = \sum_{j \neq i} e^{-\eta_2(r_{ij}-\beta s_0)}. \quad (3.9)$$

As shown in equation (3.3), the atomic sphere correction is the difference between the actual system pair potential and the reference system pair potential. As the reference system is the fcc crystal, its pair potential is the sum over only the 12 nearest neighbors, so that

$$\Delta E_{AS} = -\frac{1}{2} \left[ 12V(\beta s) - \sum_{j \neq i} V(r_{ij}) \right], \quad (3.10)$$

and the pair potential is then

$$V(r) = -V_0 e^{-\kappa \left( \frac{r}{s_0} - s_0 \right)}. \quad (3.11)$$
From equation 3.10 and 3.11 we find that the atomic sphere correction becomes:

$$\Delta E_{AS} = -6V_0e^{-\kappa(s-s_0)} + \frac{1}{2}V_0 \sum_{i \neq j} e^{-\kappa(\frac{r}{\beta}-s_0)}, \quad (3.12)$$

$$\Delta E_{AS} = -6V_0 \left[ e^{-\kappa(s_i-s_0)} - \frac{\sigma_{2,i}}{12} \right], \quad (3.13)$$

where $\sigma_{2,i}$

$$\sigma_{2,i} = \sum_{i \neq j} e^{-\kappa(\frac{r_{ij}}{\beta}-s_0)}. \quad (3.14)$$

The cohesive energy is also a function of the neutral sphere radius, which we assume has the form

$$E_{c,i}(s_i) = E_0f \left[ \lambda (s_i - s_0) \right], \quad (3.15)$$

where $f = (1 + x)e^{-x}$. [2]

We have shown how the EMT potential is parameterized for mono-atomic systems, but as will be shown in the following chapters, the present work is focused on binary alloys. For binary systems, the cohesive energy of each atom depends again on $E_0$, $\lambda$, and $s_0$, which will be different for each element. If we call the two elements $A$ and $B$, then the cohesive energy of $A$ type atoms will depend on parameters $E_{0A}$, $\lambda_A$, and $s_{0A}$, and for $B$ type atoms on $E_{0B}$, $\lambda_B$, and $s_{0B}$. As mentioned in the calculations for the mono-atomic system, the total energy of the reference system is determined by the embedding density $n$ which is dependent on $s$ (equation 3.7). For the case of a binary system, the neutral sphere radius for type $A$ atoms has the form

$$s_A = s_{0A} - \frac{1}{\beta \eta_{2A}} \log \frac{1}{12} (\sigma_{1AA} + \chi_{AB}\sigma_{1AB}), \quad (3.16)$$

where $\chi_{AB} = n_{0B}/n_{0A}$ is a scale factor, assuming $\eta_{1A} = \eta_{1B}$. The atomic sphere correction for type $A$ elements is then

$$\Delta E_{AS}^A = \sum_{jA \neq i} V_{AA}(r_{ijA}) + \chi_{AB} \sum_{jB \neq i} V_{AB}(r_{ijB}) - 12V_{AA}(\beta s_{1A}). \quad (3.17)$$
Previously, the parametrization of the EMT potential for the mono-atomic and binary systems was made assuming that the reference system is an fcc crystal and only the 12 nearest neighbors contribute to the density. To account for more than just nearest neighbor contributions, the sum \( \sigma_{1,i} \) (equation 3.9) may be replaced by

\[
\sigma_{1,i} = \frac{1}{\gamma_1} \sum_{j \neq i} e^{-\eta_2(r_{ij}-\beta s_0)} \Theta(r_{ij}),
\]

(3.18)

where \( \gamma_1 \) scales \( \sigma_{1,i} \) so that it still has the same value in an fcc crystal when we extend the sum beyond nearest neighbor. Here, \( \Theta(r_{ij}) \) is a cut-off function which is chosen to have the Fermi form

\[
\Theta(r_{ij}) = \frac{1}{1 + e^{a(r-r_c)}},
\]

(3.19)

where \( a \) determines the sharpness of the cut-off and \( r_c \) is the cut-off radius. Similarly, \( \sigma_{2,i} \) becomes:

\[
\sigma_{2,i} = \frac{1}{\gamma_2} \sum_{i \neq j} e^{-\kappa(r_{ij}-\beta s_0)} \Theta(r_{ij}).
\]

(3.20)

The scale factors \( \gamma_1 \) and \( \gamma_2 \) were chosen in such way to ensure \( E_c = E_{coh} \) and \( \Delta E_{AS} = 0 \) for the equilibrium reference system beyond the nearest neighbor. The given equations describe the EMT potential’s seven parameters for each element. The way these parameters are fitted will be described in the next chapter.

### 3.3 Density functional theory

Density functional theory (DFT) is a quantum mechanical method for calculating the ground state energy for many-body systems. The advantage of DFT is that it reduces a problem in terms of the many electron wave function \( \Psi(r_1, \ldots, r_n) \) into one in terms of the electron density \( n(r_1) \). This is based on the Hohenberg Kohn theorem which states that for a given external potential the ground state energy is a unique functional of the electron density, i.e. \( E_0[n] \).
\[ E_0[n] = F[n] + \int n(r) v_{ext}(r) dr \] (3.21)

where

\[ F[n] = T[n] + V_{ee}[n], \] (3.22)

\( T[n] \) is the kinetic energy, \( V_{ee} \) describes the electron-electron interaction and \( v_{ext} \) is the external potential. However, an exact form for \( F[n] \) in terms of the density is unknown. Instead, we rewrite \( F[n] \) in the form:

\[ F[n] = T[n] + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} n(\mathbf{r}) v_{xc}[n(\mathbf{r})](\mathbf{r}) \] (3.23)

where \( v_{xc} \) is the exchange correlation potential which gives the correct electron-electron interaction \( V_{ee} \). This potential includes corrections to the Coulomb potential so that the Pauli exclusion principle is satisfied, electron-electron correlations, and self interactions corrections. In practice the most common implementation of DFT utilizes the Kohn-Sham method. Here, we assume a form for \( v_{xc} \), and then solve the non-interacting Schrödinger equation

\[ i \frac{\hbar^2}{2} \nabla^2 \Psi_i + v(\mathbf{r}) \Psi_i = E_i \Psi_i, \] (3.24)

with a potential \( v[n(\mathbf{r})] = v_H[n] + v_{xc}[n] + v_{ext}(\mathbf{r}) \), which depends on the density \( n = \sum \Psi_i^* \Psi_i \), in a self consistent manner.

We use DFT in order to obtain parameters (lattice constants, formation energies, elastic constants), which we need to fit the EMT interatomic potential. These parameters were calculated only for the crystalline structures that are presented in chapter \( \text{[4]} \). The calculations were done using the GGA functional PW91 \( \text{[43]} \), a wave function cutoff of 350 eV, and a density cutoff of 450 eV. We also used a grid of 8 \( k \)-points sampling in each direction.

The total energy of the system was calculated by varying the lattice constant \( a \). The lattice constant for each structure was chosen around equilibrium, when the energy reaches a minimum. From the energy versus lattice constant plot we calculate \( \frac{d^2 E}{da^2} \), which we used to calculate the bulk modulus

\[ B = V \frac{d^2 E}{dV^2} = \frac{1}{9a} \frac{d^2 E}{da^2}. \] (3.25)
3.4 Molecular dynamics. Equation of motion integration

The most time consuming part of Molecular Dynamics simulations is typically the calculation of the force acting on every atom. In our case, we have to consider the contribution to the force on an atom \( i \) from all its neighbors. Once we have computed the forces between the atoms, we then integrate Newton’s equation of motion

\[
m \frac{d^2 r_i}{dt^2} = \sum_{j \neq i} F(r_{ij}).
\] (3.26)

To integrate \(3.26\) we use a velocity Verlet algorithm [44], which has proved to be one of the simplest and most efficient [45, 46]. We consider an atom \( i \) of mass \( m \) at time \( t \), and using the velocity Verlet algorithm we may compute the new positions \( r_i(t + \Delta t) \) and velocity \( v_i(t + \Delta t) \) after a time step \( \Delta t \) as:

\[
r_i(t + \Delta t) = r_i(t) + v_i(t) \Delta t + \frac{F_i(t)}{2m} \Delta t^2,
\] (3.27)

\[
v_i(t + \Delta t) = v_i(t) + \frac{F_i(t + \Delta t) + F_i(t)}{2m} \Delta t,
\] (3.28)

where \( F_i(t) \) is the force that acts on the \( i \)th atom at a time \( t \).

3.5 Energy minimization

The goal of energy minimization is to find a route from an initial configuration to the nearest minimum energy conformation using as few calculations as possible. The energy minimization is very important for an analysis of Molecular Dynamics, where after a simulation is completed, the configuration is used as the starting configuration for energy minimization. The minimization algorithm should give the best structure for each configuration. The energy minimization can be done using various algorithms, some of which are very briefly described here, with special emphasis on their applicability to metallic glasses.
3.5.1 Molecular dynamics minimization

In our simulations, we used a velocity Verlet algorithm to integrate the equations of motion and ran our MD algorithm, stopping the atoms when they moved away from a minimum. This algorithm is implemented in our ASAP program from the CAMd Open Software project [47] as the MDmin algorithm [48]. First we evaluate \( p_i(t) \cdot F_i(t) \), where \( p_i(t) \) is the momentum at time \( t \). If \( p_i \cdot F_i(t) > 0 \) it means that the atom is approaching a local minimum for the potential energy. If \( p_i \cdot F_i(t) \) becomes zero (meaning that the atoms is near the minimum for the potential energy) or negative then we zero the momentum. This means that we remove the system’s kinetic energy, which will be close to its maximum.

3.6 Langevin dynamics

The methods described previously allow us to perform Molecular Dynamics, but in the absence of temperature. However, we need to be able to perform our simulation at finite temperature. In order to do this, we use Langevin Dynamics, which we consider to be a suitable thermalization algorithm for the calculations in the present work. The idea behind Langevin dynamics [48, 49] is to add two additional terms to Newton’s second law, which let the system interact with a temperature reservoir. The Langevin equation is then:

\[
\frac{d^2 r_i}{dt^2} = F_i(t) + \mathbf{R}_i(t) - \gamma v_i. \tag{3.29}
\]

The last term added to Newton’s law represents a frictional force \( \gamma v_i \), where \( \zeta = \gamma/m \) is the friction coefficient, while the other term \( \mathbf{R}_i(t) \) is a random force. We require that the friction coefficient is related to the fluctuations of the random force by the fluctuation-dissipation theorem, so that

\[
\langle \mathbf{R}(t) \cdot \mathbf{R}(t') \rangle = 2\zeta k_B T \delta(t - t'). \tag{3.30}
\]

In equation 3.30, the terms on the left side have been averaged over time \( t \), \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature. The energy that the
system loses through friction is compensated by the random force, $R(t)$. If
the energy gets too high, then the friction term becomes dominant and the
system loses energy. The Langevin algorithm is more time-consuming than
the Verlet one, and it involves the choice of a friction coefficient, which for
this work was chosen to be $\zeta = 0.1$. 
Chapter 4

EMT Interatomic Potential for CuZr

CuZr has recently been discovered to be a binary bulk metallic glass \[50, 51\]. Since binary alloys are easier to model than alloys with more elements, this makes CuZr an attractive bulk metallic glass to study theoretically. The quality of the results obtained will depend on the quality of the interatomic potential, with simple potentials giving a less accurate description of the interatomic interactions while allowing very large simulations, and more complicated potentials giving a better description of the interaction, but limiting the simulation size. Many-body potentials, such as the Embedded Atom Method \[29\] and the Effective Medium Theory (EMT) \[22, 21\], have been shown to give a good description of late transition metals, and their alloys yielding crystallization in close-packed structures while still allowing simulations with millions of atoms \[52\]. In this chapter, we will discuss an EMT potential optimized for modeling the mechanical and thermodynamic properties of CuZr bulk metallic glass.

Previously, an interatomic force field has been fitted to CuZr by Duan et al., but we find that the EMT force field described here provides a better description of the structure of the metallic glass. The potential developed here will be used to model the mechanical properties of CuZr, which are discussed in the following chapters.
<table>
<thead>
<tr>
<th>Property</th>
<th>Optimized value</th>
<th>Target value</th>
<th>Difference</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Shear Modulus</td>
<td>0.511477</td>
<td>0.511</td>
<td>0.000477</td>
<td>0.1%</td>
</tr>
<tr>
<td>Cu Bulk Modulus</td>
<td>0.889516</td>
<td>0.886</td>
<td>0.003516</td>
<td>0.4%</td>
</tr>
<tr>
<td>Cu C_{11}</td>
<td>1.093305</td>
<td>1.100</td>
<td>-0.00695</td>
<td>0.6%</td>
</tr>
<tr>
<td>Cu Cohesive Energy</td>
<td>3.521416</td>
<td>3.510</td>
<td>0.011416</td>
<td>0.3%</td>
</tr>
<tr>
<td>Cu Lattice Constant</td>
<td>3.587869</td>
<td>3.610</td>
<td>-0.02131</td>
<td>6.1%</td>
</tr>
<tr>
<td>Zr Shear Modulus</td>
<td>0.141930</td>
<td>0.150</td>
<td>-0.008070</td>
<td>5.4%</td>
</tr>
<tr>
<td>Zr Bulk Modulus</td>
<td>0.474796</td>
<td>0.440</td>
<td>0.034796</td>
<td>7.9%</td>
</tr>
<tr>
<td>Zr Cohesive Energy</td>
<td>6.300625</td>
<td>6.300</td>
<td>0.000625</td>
<td>0.0%</td>
</tr>
<tr>
<td>Zr Lattice Constant</td>
<td>4.570</td>
<td>4.552</td>
<td>-0.017120</td>
<td>0.4%</td>
</tr>
<tr>
<td>CuZr Shear Modulus</td>
<td>0.306406</td>
<td>0.276</td>
<td>0.030406</td>
<td>11.0%</td>
</tr>
<tr>
<td>CuZr Bulk Modulus</td>
<td>0.666679</td>
<td>0.751</td>
<td>-0.084321</td>
<td>11.2%</td>
</tr>
<tr>
<td>CuZr Formation Energy</td>
<td>-0.139429</td>
<td>-0.140</td>
<td>0.000571</td>
<td>0.4%</td>
</tr>
<tr>
<td>CuZr Lattice Constant</td>
<td>3.192319</td>
<td>3.280</td>
<td>-0.087681</td>
<td>2.7%</td>
</tr>
</tbody>
</table>

Table 4.1: Properties used in fitting the potential. Elastic constants are in eV/Å³, energies are in eV/atom and lattice constants are in Å. All values for CuZr refer to the B2 structure. The first five values (for pure Cu) were not used in the fitting in this work, but are provided for reference. All values for Zr and CuZr were obtained from DFT calculations, except the Zr cohesive energy [53] and CuZr formation energy [54, 55], which were obtained from experiments. See Paper I.

4.1 Fitting the EMT interatomic potential for CuZr

In the previous chapter, we have described the functional form of EMT and its use of seven parameters for each atomic element. Two of these parameters describe the contribution of each atom to the local electron density in its neighborhood. These are $n_0$, which describes the magnitude of this contribution, and $\eta_2$, which is the inverse decay length. The EMT parameters $s_0$, $\lambda$ and $E_0$ describe the position of the minimum, the curvature, and the
depth of the energy function of the atoms, respectively. The pair potential function is described by the parameters $V_0$ and $\kappa$, which is also an inverse decay length. In order to get the EMT interatomic potential for CuZr, we need to fit these seven parameters for each element. The parameters for Cu have been calculated previously [32], so that we may simply calculate the parameters for Zr, while keeping the ones for Cu fixed. We do this fitting by minimizing an error function

$$f(\{p\}) = \sum_i q_i \cdot |C_i^{EMT}(\{p\}) - C_i^{target}|^2,$$

(4.1)

where $\{p\} = \{s_0, n_0, E_0, V_0, \eta_2, \lambda, \kappa\}$ is the list of parameters that need to be fitted, $q_i=1$ are normalizing constants, and $C_i^{EMT}$ and $C_i^{target}$ are the EMT values (obtained from molecular dynamics) and target values (from experiment or from DFT calculations), respectively. The sum goes over the different properties used to fit the potential, such as lattice constants, cohesive energies, and elastic constants for Cu, Zr and the CuZr alloy in the B2 (or CsCl) structure, as shown in table 4.1.

The target values were obtained from quantum mechanical calculations using DFT within the generalized gradient approximation (DFT-GGA), with the Perdew-Wang 91 exchange-correlation functional [43]. Details about the method may be found in chapter 2. Calculations were performed with the DACAPO program from the CAMd Open Software project [47]. The usual care was taken to ensure convergence with respect to the plane wave cutoff,

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_0$</td>
<td>2.67</td>
<td>1.78</td>
</tr>
<tr>
<td>$E_0$</td>
<td>-3.51</td>
<td>-6.3</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>3.693</td>
<td>2.247</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>4.943</td>
<td>3.911</td>
</tr>
<tr>
<td>$V_0$</td>
<td>1.993</td>
<td>2.32</td>
</tr>
<tr>
<td>$n_0$</td>
<td>0.0637</td>
<td>0.031</td>
</tr>
<tr>
<td>$\eta_2$</td>
<td>3.039</td>
<td>2.282</td>
</tr>
</tbody>
</table>

Table 4.2: EMT parameters from Paper I.
number of k-points etc. The reason why we used data from DFT calculations to fit our potential was that is has been shown previously that this calculation may accurately describe lattice properties [56], for example in Fig. 4.1 a good agreement is shown between the calculated and experimental results for the heat of formation in the case of binary alloys.

For fitting the interatomic potential parameters, we use a downhill simplex method [57] for optimizing the function $f(\{p\})$ described above (4.1). This method requires only evaluations of the functions and not their derivatives when finding the minimum for more than one independent variable.

The result of the fit is shown in table 4.1 showing how well the target values were fitted, while table 4.2 shows the resulting EMT parameters for Cu and Zr.

### 4.1.1 Downhill simplex method in multi-dimensions

The Downhill Simplex method is a general algorithm for performing local minimizations. The method only requires evaluations of the function and
not its derivatives. This is done using a simplex.

A simplex is a geometrical figure consisting of \( N \) dimensions, \( N + 1 \) points and all their interconnecting line segments, polygonal faces etc. A simplex is a triangle in two dimensions and in three dimensions it is a tetrahedron. Although this method requires a substantial amount of time to find these minima, it is computationally efficient, stable, and easy to implement [58].

The local minimum is determined by performing a set of operations on the simplex \([4.2]\) according to a set of rules. The Downhill Simplex method takes a number of steps, most of them moving the point of the simplex where the function has the highest value through the opposite face of the simplex to a lower point (this steps is called reflection). When it can do so, the method expands the simplex in one direction to take larger steps. When it can no longer reflect or expand, the method contracts itself in the transverse direction, (this step is called contraction). When it cannot do any of the operations described above, it means that the function is close to a local minimum and the method contracts itself around it.

At the algorithm’s completion, the simplex is contracted around the local minimum, as described in Fig. \([4.2]\)

### 4.2 Testing the EMT interatomic potential

Before using the potential obtained in the previous sections, it is important to test its ability to predict properties not used in the fitting procedure. Since the intended application is CuZr metallic glasses, the potential is both tested on ordered alloys with the same composition, and on thermodynamical and structural properties of the metallic glass.

#### 4.2.1 Formation energies and lattice constants for CuZr crystalline structures. DFT versus EMT

The first test consists of comparing the formation energies and lattice constants (here expressed as a volume per atom) for four different ordered alloys.
Figure 4.2: Possible operations for a step in the simplex method. Here the simplex is a tetrahedron. The operations on a simplex can be (a) a reflection away from a high point, (b) a relaxation and expansion away from the high point, (c) a contraction along one dimension from the high point, or (d) a contraction along all dimensions towards the low point.

The stable crystal structure for Cu$_{50}$Zr$_{50}$ is the B2 (or CsCl) structure (see Fig. 4.3) but the other structures we will consider, the B1, L1$_0$, and L1$_1$, as depicted in Fig. 4.3 do not exist in nature.

However, the other structures may be set up in the computer, and the energies and lattice constants can be compared to more accurate DFT calcula-
4.2.2 MD and glass transition

A more relevant test is to examine how this potential performs for a metallic glass. Therefore we prepared a CuZr metallic glass in order to compare the glass transition temperature and the short-range order by the radial distribution function to experiment.

We performed MD simulations in order to obtain the CuZr glass phase from
Table 4.3: Comparison between DFT and EMT results for different crystal structures for Cu$_{50}$Zr$_{50}$. The B2 structure was used in the fitting of the potential, the other structures are tests of the potential.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_{\text{form}}$ (eV/atom)</th>
<th>$V$ (Å$^3$/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$ B1 (DFT-GGA)</td>
<td>0.275</td>
<td>19.57</td>
</tr>
<tr>
<td>(EMT)</td>
<td>0.203</td>
<td>18.60</td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$ B2 (DFT-GGA)</td>
<td>-0.1202</td>
<td>17.64</td>
</tr>
<tr>
<td>experiment[54]</td>
<td>-0.14</td>
<td>—</td>
</tr>
<tr>
<td>(EMT)</td>
<td>-0.139</td>
<td>16.38</td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$ L1$_0$ (DFT-GGA)</td>
<td>-0.035</td>
<td>17.23</td>
</tr>
<tr>
<td>(EMT)</td>
<td>-0.0011</td>
<td>17.23</td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$ L1$_1$ (DFT-GGA)</td>
<td>0.250</td>
<td>18.01</td>
</tr>
<tr>
<td>(EMT)</td>
<td>-0.1295</td>
<td>18.25</td>
</tr>
</tbody>
</table>

Figure 4.4: CuZr glass system: a) 2048 atoms and b) 42600 atoms.

the melt. We used two different system sizes, starting from body-centered cubic crystals of 2048 and 42600 atoms with the sites randomly occupied by Cu and Zr. The resulting glassy systems were cube-shaped with side lengths of 3.3 nm and 9.1 nm, respectively. The systems, shown in Fig. 4.4, were cooled from 1400 K (well above the melt temperature) in steps of 25 K, with
Figure 4.5: Specific heat versus temperature for two different sizes of CuZr metallic glass system during annealing. Inset: Enthalpy versus temperature for the 2048 atoms system.

an average cooling rate of 0.54 K/ps. Each temperature step begins with a short period of Langevin dynamics \[49\] to thermalize the system to the new temperature, followed by a simulation with constant \((N, P, T)\) dynamics, using a combination of Nöse-Hoover and Parrinello-Rahman dynamics \[59, 60\]. The prethermalization with Langevin dynamics is necessary to prevent oscillations in the temperature otherwise seen when the temperature of a Nöse-Hoover simulation is changed abruptly. During the constant \((N, P, T)\) dynamics we recorded the averages of different quantities of interest. These included the pressure, volume, kinetic energy, and potential energy of the system, which were used to perform the thermodynamics analysis \[32\]. The simulations were performed using the ASAP program from the CAMd Open Software project \[47\].

When plotting the enthalpy versus temperature (inset of Fig. 4.5), we observe a change in the slope near 600–700 K which indicates the glass transition.
From this slope the heat capacity $C_p$ versus temperature curve may be obtained, as shown in Fig. 4.5, since the specific heat is the derivative of the enthalpy with respect to temperature. The change in the heat capacity indicates the glass transition, $T_g$. We extracted the glass transition temperature by taking the centered derivative of $C_p(T)$, and choosing the maximum $[32]$. $T_g$ was estimated to be 620 K, compared to the experimental value of 670 K $[12]$. This good agreement is encouraging, in particular when one considers that no thermodynamical data or data on glasses was used to fit the potential.

### 4.2.3 Radial distribution function and coordination numbers for CuZr metallic glass

The radial distribution function (RDF) analysis is a standard method for obtaining information about the structure of systems, especially for liquids and amorphous structures. We calculate the radial distribution function $[63]$ as:

$$g(r)dr = \frac{dN_A}{\rho_A \cdot V}$$  (4.2)

where $dN_A$ is the number of atoms of type $A$ inside a spherical shell of thickness $dr$ at a distance $r$ from a chosen atom Fig. 4.6. $\rho_A$ is the density of $A$ atoms in the considered system, and $V$ is the volume of the shell between
Figure 4.7: Radial distribution functions $g(r)$, for CuCu, CuZr, and ZrZr metallic glasses.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Method</th>
<th>$R(\text{Å})$ CuCu</th>
<th>$R(\text{Å})$ CuZr</th>
<th>$R(\text{Å})$ ZrZr</th>
<th>N CuCu</th>
<th>N CuZr</th>
<th>N ZrZr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$</td>
<td>This work</td>
<td>2.56</td>
<td>2.75</td>
<td>3.13</td>
<td>4.44</td>
<td>6.24</td>
<td>7.59</td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$</td>
<td>EXAFS [61]</td>
<td>2.57</td>
<td>2.84</td>
<td>3.19</td>
<td>4.10</td>
<td>5.4</td>
<td>7.40</td>
</tr>
<tr>
<td>Cu$<em>{50}$Zr$</em>{50}$</td>
<td>XRD [62]</td>
<td>2.68</td>
<td>2.80</td>
<td>3.16</td>
<td>4.60</td>
<td>4.8</td>
<td>7.80</td>
</tr>
<tr>
<td>Cu$<em>{46}$Zr$</em>{54}$</td>
<td>Simul. [35]</td>
<td>2.67</td>
<td>2.78</td>
<td>3.22</td>
<td>3.20</td>
<td>7.6/6.5</td>
<td>9.10</td>
</tr>
</tbody>
</table>

Table 4.4: Average nearest neighbor distances and coordination numbers. The first row is this work and the next two are experimental data obtained by two different methods. The last row is from simulations by Duan et al. performed with another potential and a slightly different composition. Since Cu and Zr are present in unequal amounts, the number of Zr neighbors for a Cu atom is different from the number of Cu neighbors for a Zr atom, and two numbers are therefore given for N(CuZr).
$r$ and $r + dr$, as shown in Fig. 4.6. The volume of the shell is then given by:

$$V = \frac{4}{3} \pi (r + dr)^3 - \frac{4}{3} \pi r^3 \approx 4 \pi r^2 dr. \quad (4.3)$$

If we consider the number of particles per unit volume to be $\rho$, then the total number of atoms in the shell is $4 \pi \rho r^2 dr$, and the number of atoms in the volume element varies as $r^2$, so that

$$\int_0^\infty g(r) 4 \pi r^2 dr = N - 1 \approx N. \quad (4.4)$$

In Fig. 4.7 we show partial RDF $g_{\text{Cu-Cu}}$, $g_{\text{Cu-Zr}}$ and $g_{\text{Zr-Zr}}$ at the glass transition temperature. The first peak of the RDF indicates the average distance at which we find nearest neighbor atoms, with $g_{\text{Cu-Cu}}$ and $g_{\text{Zr-Zr}}$ yielding the distance between like atoms, and $g_{\text{Cu-Zr}}$ the distance between unlike atoms. By integrating the RDF given in eqn. 4.4 until the first minimum, we obtain the number of nearest neighbors atoms for Cu and Zr atoms. The results are summarized in table 4.4 with comparison with other experimental and simulation data. The values for the coordination numbers are in good agreement with the experimental ones.

As a final test, we have compared the bulk and shear modulus with experimental values. Our calculated values were obtained at zero temperature by applying strain in the elastic limit and relaxing the structure at each strain step. We obtain 108.69 GPa and 29.25 GPa, compared to the experimental values 101.2 GPa and 31.3 GPa [12], respectively, with a deviation of less than 8%.
Chapter 5

Shear Deformation

Plastic deformation of metallic glasses at room temperature occurs through the formation and evolution of shear bands in which it is localized. This chapter contains details about simple shear simulations performed in order to investigate the formation of shear bands and to measure their widths. Shear bands have been seen to form above a certain shear strain in both CuZr and CuMg under shear deformation. Details about the simulation method and results will follow in the next section.

The width of a shear band may be measured as the characteristic width of the displacement profile as shown in Fig. 5.1. Experimentally, shear bands are identified as sharp surface steps when they are observed in scanning electron and atomic force microscopies [64]. Transmission electron microscopy (TEM) is used to measure the width of the shear bands, for example the width of a shear band measured using TEM was found to be 20 nm in a Pd$_{80}$Si$_{20}$ glass [65], 10-20 nm in a Fe$_{40}$Ni$_{40}$B$_{20}$ [66] and even $\leq$ 10 nm in a Zr$_{56.3}$Ti$_{13.8}$Cu$_{6.9}$Ni$_{5.6}$Nb$_{5.0}$Be$_{12.5}$ [67]. But there are difficulties in characterizing the width and the structure of the shear bands using a TEM [66]. Image interpretation is complicated by projection effects and the surface relief of the TEM foils due to the shear offset along the band [64].

Another way to study the formation and the properties of shear bands is through molecular dynamics simulations. Molecular dynamics simulations
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Figure 5.1: Schematic displacement profile (solid curve) across a shear band between two rigid blocks of metallic glass moving relative to each other (arrows). Structural changes are found in the shaded band where the shear and the shear rate are highest. The profile of the temperature rise around the band has a width much greater than the shaded band thickness. Reproduced from Zhang and Greer [64].

of a Mg₈₅Cu₁₅ model binary glass structure and deformation mechanism do show shear localization. The simulations were carried out in this case by using an EMT interatomic potential. The width of the shear bands could then be measured during a simulated uniaxial deformation [34]. The shear bands were identified by examining for each atom the residual displacement $D_{\text{min}}^2$ [6]. The $D_{\text{min}}^2$ profile of the shear band has a width of 10 nm and is independent of the strain rate [34].

Ogata et al. [68] used a Lennard Jones potential to simulate simple shear deformations on Cu₅₇Zr₄₃. During shearing both shear localization and shear band nucleation were observed. Fig. 5.2 shows the inelastic displacement of each atom in the $x$ direction for a 532 Å×532 Å×32 Å sample. The average displacement in the $x$-direction shows that the localization is initiated at different $z$ positions and for strains larger than 8%. Once the shear localization takes place at a $z$ position, the $z$ position does not change in the next steps [68]. Above 15% , the stress-strain curves become flat because all additional work is dispersed by sliding of the shear bands [68].
Figure 5.2: Average atomic displacements in the x direction for 9% affine strain averaged over different z-slices for a Cu$_{57}$Zr$_{43}$ glass sample with geometry as shown in inset. Shear localizations are seen at strains higher than 8%. The localization is initiated at different z positions. Reproduced from Ogata et al. [68].

5.1 Simple shear deformation of CuZr and CuMg. Simulation method and results

To study the formation of shear bands, we deformed the metallic glasses under simple shear, using the geometry illustrated in Fig. 5.3. The sample is divided into three parts, two outer “walls” of 3 nm thickness, and a central region. In the central region, the dynamics of the atoms is left unperturbed, but in the two walls the center of mass motion is constrained, so that the two walls move with a constant speed relative to each other. The atoms in the walls are not held rigid, they can still move with respect to each other,
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Figure 5.3: Geometry of the Cu_{50}Zr_{50} and Cu_{15}Mg_{85} glass samples undergoing shear deformation using an EMT interatomic potential.

only the sum of their velocities is held fixed. By causing one wall to move in the \( y \)-direction, a shear deformation with constant shear rate is applied to the system. The system has periodic boundary conditions in the \( y \) and \( z \) directions, but free boundaries in the \( x \) direction. The shear simulation are done at constant temperature of 50K.

During the deformation, velocity profiles (average atomic velocities as a function of \( x \)-coordinate) are calculated. Both velocity profiles and plots of the deformed system clearly show the formation of shear bands (see Fig. 5.4). The width of the shear bands, evaluated from visual observations, are 5 nm for the CuZr glass, and 10 nm for the CuMg glass. The latter is consistent with the simulations of Bailey et al. [34]. A better estimate can be obtained by fitting the velocity profiles to a Fermi function \( 1/(\exp(x/\alpha)+1) \) or to the \( \arctan(x/\alpha) \) function, as explained in PaperII. At the same time, it has been observed before that the shear bands tend to be thinner in harder alloys [64]. In Fig. 5.4 the temperature profile during shearing shows the temperature increases in the shear band region. We also find that the profile of raised temperature around the band has a width greater than the shear band width [64].
Figure 5.4: Velocity and temperature profiles (average atomic velocities and temperatures as a function of x-coordinate) for Cu$_{50}$Zr$_{50}$ and Cu$_{15}$Mg$_{85}$ glasses.
Chapter 6

Nanoindentation

Since nanoindentation is a good method for testing mechanical properties of materials in small volumes (see chapter 1) we performed simulated nanoindentation on Cu_{0.50}Zr_{0.50} and Mg_{0.85}Cu_{0.15} metallic glasses in order to study the formation of shear bands. During nanoindentation, shear bands were seen to form under the nanoindenter, their formation and propagation being influenced by different parameters. These were indentation velocity, radius of the indenter, cooling rate and material compositions, see Paper II. The simulation method and the results will be discussed in this chapter. For comparison we performed nanoindentation on a Cu crystal which will be discussed in this chapter as well, see Paper II.

6.1 Simulation method

In 2005 Shi and Falk [28] proposed a model for simulating nanoindentation. They performed simulated nanoindentation on a two dimensional model binary alloy. The alloy consists of two species called S and L for small and large with composition \( N_L : N_S = (1 + \sqrt{5}) : 4 \). The atoms interacted via a Lennard-Jones potential of the form:

\[
\Phi_{ij} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], \quad (6.1)
\]
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where $\varepsilon$ is the bonding energy, $\sigma$ provides a length scale and the bond energy $\varepsilon_{SS} = \varepsilon_{LL} = 1/2\varepsilon_{SL}$. Details about the choice of the system and the Lennard Jones potential parameters can be found in [28, 6]. The samples consisted of 200,000 atoms cooled with different cooling rates [28, 69]. The indenter was modeled by imposing a purely repulsive potential of the form:

$$\Phi_{II} = \varepsilon \left[\frac{r_{II} - R_I}{0.6\sigma_{SL}}\right]^{-12},$$

(6.2)

where $r_{II}$ is the distance between atoms $i$ and the center of the spherical indenter of radius $R_I$ (=75nm) [28]. In other simulations they have used a shaped cylindrical indenter [69]. The indenter is modeled in such a way that it has no surface friction and is lowered into the glassy sample under displacement control as shown in Fig. 6.1.

![Figure 6.1: Illustration of the nanoindentation testing geometry. Periodic boundary conditions (PBC) apply on the $x$–$y$ and $y$–$z$ planes, as reproduced from Shi and Falk [69].](image)

In our case, samples of metallic glass were produced by cooling Cu$_{0.50}$Zr$_{0.50}$ and Mg$_{0.85}$Cu$_{0.15}$ systems from 1400 K (above the melting temperature) down to 40 K, with a cooling rate of 0.54 K/ps. Details about the cooling and glass forming procedure were given previously in chapter 3. The glassy systems obtained have dimensions of 52.9 nm $\times$ 52.9 nm $\times$ 1.6 nm for CuZr and 57.2 nm $\times$ 57.2 nm $\times$ 1.7 nm for CuMg, both corresponding to 270,000 atoms.
Before nanoindentation, the samples are repeated in the $x$ direction, giving a CuZr sample size of $105.9 \, \text{nm} \times 52.9 \, \text{nm} \times 1.6 \, \text{nm}$ and a CuMg sample size of $114.4 \, \text{nm} \times 57.2 \, \text{nm} \times 1.7 \, \text{nm}$ with periodic boundary conditions along the $x$ and $z$ directions, and free boundaries in the $y$ direction.

In order to perform simulated nanoindentation, we perform molecular dynamics at constant temperature using Langevin dynamics \[49\] at constant temperature $116\text{K}$, while the indenter is modeled as a repulsive potential as proposed by Shi and Falk \[28\] and described previously. The form of our repulsive potential is:

$$E = c(r - R)^{-6},$$

where $r$ is the distance from the center of the indenter and $R$ is the indenter radius. The strength parameter $c = 2.0 \, \text{eV}^6 \, \text{Å}$. The indenter is lowered into the substrate under displacement control, recording at each step the load and the total displacement. Since the samples are very thin in the $z$ direction, the simulation is quasi two-dimensional, and we choose to use a cylindrical indenter. During indentation, the lower edge of the system is held fixed by fixing the positions of the atoms in the bottom 0.8 nm of the system. The thickness of the system is kept constant during the indentation (plane strain), as discussed in Paper II.

To visualize the plastic flow and the localization of the shear bands we use the $D_{min}^2$ method introduced by Falk and Langer \[6\]. According to this method, $D_{min}^2$ is the local deviation from an affine deformation during a time interval of time between a pair of configurations $[t - \Delta t, t]$. Specifically, $D_{min}^2$ represents the residual displacement differences unaccounted for by the best fit strain matrix for an atom. With this quantity defined for all atoms, we are doing a coarse graining of the system, dividing it into boxes within each the average $D_{min}^2$ is computed.

Another method that we used to visualize the plastic flow and the localization of the shear bands is the so called “stripe painting” method \[34\]. In this case, the undeformed configuration is taken and all atoms are binned according to their $y$ position, and those in odd bins are labeled “black”. This designation is maintained throughout the deformation \[34\].
6.2 Shear band formation

A nanoindentation simulation is performed on the CuZr sample as described above. The cylindrical indenter with a diameter of 30 nm, is indented into the sample with a velocity of 7 m/s, as illustrated in Fig. 6.3.

As the shear is inhomogeneous, it is not possible to rigorously define an equivalent shear rate. However, it corresponds roughly to a shear rate on the order of $10^8$ s$^{-1}$ (a homogeneous shear rate of $10^8$ s$^{-1}$ would correspond to the ends of the sample moving with a relative velocity of 10 m/s).

We visualized the plastic flow under the indenter with the $D_{\text{min}}^2$ method and “stripe painting” method, both described previously. As it can be observed from Fig. 6.2, $D_{\text{min}}^2$ is a better method to visualize the plastic flow for this kind of deformation. However, the “stripe painting” method confirms that atom shearing is happening, and the regions where atoms are shearing correspond with the regions where shear bands are identified by $D_{\text{min}}^2$. 

Figure 6.2: Shear band visualization using a) $D_{\text{min}}^2$ method, b) and c) “stripe painting” method. We highlight the shear bands location observed in b) and c) by blue lines which match the more clearly visible shear bands seen in a).
Figure 6.3: Development of shear bands during nanoindentation on a Cu-Zr thin sample: a-d) visualization of strain localization at a 24 Å, 32 Å, 42 Å and 52 Å depth of the indenter, the indentation velocity was 7 m/s; e) The lower curve is the corresponding load displacement curve, the displacements corresponding to the four panels are shown with arrows. It is seen that the shear bands are forming gradually, there is no correspondence between events on the indentation force curve and formation of shear bands. The upper curve is a similar indentation when the indentation velocity is increased to 30 m/s, as reproduced from Paper II.

During nanoindentation, the net force on the indenter is recorded as a function of indentation depth, see figure 6.3. The curve is not smooth, but contains small serrations, presumably reflecting individual events during de-
formation, as discussed in Paper II. It would be tempting to interpret this as the formation of individual shear bands, but that interpretation is not supported by direct visualization of the shear band formation. As is seen in figure 6.3, the shear bands are not formed at once, but grow gradually during the nanoindentation.

The shear bands are less clearly formed than in the simulations of Shi and Falk [28]. The simulations cannot, however, be directly compared, as the simulations of Falk and Shi are two dimensional and use a Lennard-Jones model potential, whereas our simulations have a finite (but small) thickness, and use a more realistic (but also complex) potential. The more complicated potential combined with the larger number of atoms due to the finite thickness, leads to a much larger computational burden, so that our indentations are therefore necessarily done with higher indentation velocities. There are thus three major differences between these simulations and the simulations by Shi and Falk. These are in dimensionality, the potential and the indentation speed, and it is not surprising that our results are significantly different. Shi and Falk lower their indenter into the samples with a velocity of 0.3 m/s with the samples called Sample I, Sample II and Sample III according to the cooling rates they have obtained.

The cooling rates they use are \( \approx 0.06 \times 10^{-2} \) K/ps for Sample I, \( \approx 0.03 \) K/ps for Sample II. The third sample was cooled instantaneously by rescaling the particle velocities and then allowing them to age for 100\( t_0 \) (\( t_0 = 1 \) ps).

Figure 6.4 shows the plastic flow under the indenter for samples I, II and III. In Sample I a few shear bands carry the plastic flow while in Sample II, the majority of the deformation is happening in the region immediately beneath the indenter and the plastic flow is more evenly distributed with smaller spacing between the bands. Sample III exhibits deformation at a finer scale then the other samples, with shear band spacing less than half that in Sample I.
Figure 6.4: Visualization of the magnitude of the local deviatoric shear strain under the indenter at maximum depth in three samples produced at different quench rates [28]. Dark regions denote regions of high strain. The scale bar in the upper right of the image is approximately 25 nm, as reproduced from [28].

6.3 Influences on shear band formation

In this section we study how the shear band formation is influenced by varying the parameters of the nanoindentation. This corresponds to the varying of physical parameters during a nanoindentation experiment. We vary the indenter velocity, its radius, the cooling rate during glass formation and the composition of the glass. All modifications are relative to a “standard sim-
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Simulation of a CuZr metallic glass produced at a cooling rate of 0.44 K/ps, indented with a cylindrical indenter with radius 30 nm and indentation velocity 7 m/s. Fig. 6.5 shows how the shear band formation is influenced by the indentation velocity. Here, a simulation with an indentation velocity of 30 m/s is compared with the reference simulation. The shear band formation is less obvious in the fast indentation. A clear indentation rate dependency of the load displacement curve is also seen. The loading force - and thus the stress in the material - is significantly higher during the fast simulation, but no qualitative differences are seen. It can be speculated that even lower indentation rates will lead to the formation of fewer and larger shear bands, and possibly lead to macroscopic failure through a few very large shear bands [70].

Figure 6.5: Influence of varying the indentation velocity on shear band formation and on load displacement curves. The indentation velocities are 30 m/s (panel a) and 7 m/s (panel b). The shear bands are less developed during the fast nanoindentation. The corresponding load displacement curves are shown in Fig. 6.3e, as reproduced from Paper II.

Schuh et al. studied the strain rate influence on the serrated flow during indenting for four different metallic glass samples [70]. Serrated flow was found to be a strong function of the rate of deformation, with more rapid indentations suppressing - and slower indentations promoting - prominent
serrations [70]. They also identified for each alloy a critical indentation strain rate above which load serrations apparently do not occur, as shown in Fig. 6.6.

Figure 6.6: Load displacement ($P - h$) curves measured on the loading portion of nanoindentation experiments, for four BMG composition investigated (Pd-40Ni-20P, Pd-30Cu-10Ni-20P, Zr-10Al-10Ni-15Cu and Zr-10Al-14.6Ni-17.9Cu-5Ti). Curves are offset from the origin for clear viewing, and the rates are specified in each graph, as reproduced from [70].

Jiang et al. [71] performed nanoindentation on Al$_{90}$Fe$_5$Gd$_5$ at different de-
formation rates. Their study shows that the deformation rate affects the number of shear bands, as shown in Fig. 6.7 and consequently the serrated flow behavior of amorphous alloys. Their observations outside of the indenter are consistent with other studies of strain rate dependence made in tensile tests [72, 73]. They conclude that a lower strain rate is required for the contribution from an individual shear band to resolved [71].

Figure 6.7: AFM illumination images of indents produced at loading rates of (a) 100 nm/s and (b) 1 nm/s, reproduce from [71].

Tensile tests demonstrated that at low strain rates, failure occurred along a
Figure 6.8: Influence of varying the indenter radius. The radii are 20 nm (a) and 30 nm (b). More shear band formation is observed under the larger indenter, as reproduced from Paper II.

In spite of the indenter diameter being an order of magnitude larger than the width of the shear band, a difference is also seen when the indenter radius is varied. This is illustrated in figure 6.8, where the effect of reducing the indenter radius by 33\% is studied. As is seen, fewer shear bands are formed when we compare situations with the same indentation depth. It is likely that this difference is at least partly caused by less material being displaced by the smaller indenter.

The effect of changing the cooling rate during the glass formation is investigated in figure 6.9, where identical nanoindentation simulations are per-
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Figure 6.9: Influence of varying the cooling rate during glass formation. Samples created with cooling rates of 2.2 K/ps (a) and 0.44 K/ps (b) were subjected to otherwise identical nanoindentation simulations. The shear localization appears stronger in the slowly cooled sample, as reproduced from Paper II.

formed on two samples produced with cooling rates of 2.2 K/ps and 0.44 K/ps. In this case, the difference is less pronounced, but the shear bands appear more distinct in the slowly cooled sample. This is consistent with results by Shi and Falk [28] showing a stronger tendency for shear localization for more gradually quenched samples, as shown in Fig. 6.4.

Finally, we investigated the consequences of replacing the CuZr glass with a CuMg glass (Fig. 6.10). Shear localization is far more pronounced in the CuZr sample. This is consistent with our previous findings that shear bands are approximately twice as wide in a CuMg glass. We also observed previously from our simulations that if the sample size and/or indenter radius are not big enough with respect to the shear band width, the clear formation of shear bands can not be observed. In this case, this may be the reason why we did not see the same clear shear localization in CuMg sample as we did in CuZr.
6.4 Nanoindentation of crystalline samples

For comparison, we subjected a nanocrystalline sample to indentation in a similar manner. Nanoindentation of nanocrystalline samples has previously been studied by Van Swygenhoven et al. \cite{74, 75}, with a particular focus on the onset of plastic deformation under a spherical indenter. In this work, we have chosen to mimic the indentation parameters used for the metallic glass, so the nanocrystalline sample is quasi-two dimensional, with $\langle 110 \rangle$-directions along the thin direction (the $z$ direction). This orientation is chosen to maximize the number of possible slip systems in the crystal, which is nevertheless still significantly lower than in a full three-dimensional simulation \cite{76}. The material for this simulation is copper, described with the EMT potential \cite{22}. Details about the sample geometry and simulations can be found in Paper II.

Figure 6.11 shows the deformation during this nanoindentation, and Fig 6.12 shows the corresponding load displacement curves. A number of noteworthy features are marked by letters on Fig. 6.11b. Right below the indenter (marked “A”), the plastic deformation is severe, and several grain bound-
Figure 6.11: Nanoindentation of nanocrystalline copper. (a) The initial configuration before indentation. Atoms in the grain interiors are not shown, atoms at stacking faults and twin boundaries are colored red, atoms in grain boundaries, dislocation cores and at surfaces are blue. Both high-angle and low-angle grain boundaries are seen, the former are shown as blue walls, the latter are seen to be made of individual dislocations. A few stacking faults created by dislocation activity during annealing are also seen. (b) After nanoindentation, significant plastic deformation has occurred, in particular just under the indenter, where numerous stacking faults and deformation twins have appeared. The letters A-F mark features discussed in the text. (c) A deformation map shows that the majority of the deformation occurs inside the grains and is caused by dislocation activity, although some grain boundary sliding is also seen. Reproduced from Paper II.
cause these to move. Many stacking faults are seen, which are caused by the high stress levels. This makes making the energy of the stacking fault irrelevant compared to the elastic energy. Another example of a low angle grain boundary disappearing as a result of dislocation migration is marked “B”.

A few grain boundaries “reconstruct” under the applied stress by emitting an array of partial dislocations (for example at “C”). Presumably, a lower grain boundary energy can be obtained and some of the applied stress relieved, by the motion of the dislocation wall at the expense of creating some stacking faults. A similar phenomenon is seen at “D”, where a wall of full dislocations has been emitted by the grain boundary. An extreme case is seen at “E”,

Figure 6.12: Load displacement curve during nanoindentation of the crystal. The insets marked a and b show the deformation occurring in the two intervals between the arrows. Reproduced from Paper II.
where a grain boundary has split into two separated by a region of (slightly faulted) HCP crystal. Similar reconstructions of grain boundaries under stress have previously been seen in computer simulations [77]. At “F” a stacking fault has been removed by the motion of a partial dislocation, and a new one has been created nearby by an independent event, creating the illusion that a stacking fault has moved.

The events discussed above can also be found in the displacement map in Fig. 6.11. The figure shows a striking difference between the deformation distributions in the glass and in the nanocrystalline sample: in the crystalline sample the spatial distribution of the deformation is much more uneven, as it is controlled by the polycrystalline structure. Deformation can only occur at grain boundaries, or where dislocations are available, typically from grain boundary sources.

The load-displacement curve in Fig. 6.12 shows significantly larger serrations than for the glassy samples. This is caused by avalanches of dislocation activity. The insets show how the deformation occurs just before and during one of the serrations. It is clearly seen that the serration does not correspond to a single dislocation event, but rather to an avalanche of events.

### 6.5 Nanocrystals embedded In glass

Cast Cu$_{50}$Zr$_{50}$ alloy rods with a diameter of 1 mm have been found to consist of a glassy phase containing fine crystalline particles with a size of about 5nm [78]. These rods were found to exhibit a high yield strength under uniaxial compression tests as shown in Fig. 6.13. A scanning tunneling electron microscopy (STEM) image obtained by Inoue et al. after the uniaxial compression test shows that the crystalline phase no longer consists of spheroidal particles, as it did initially in the undeformed sample. The particle width is elongated, which suggest that the elongated particles are formed by crystalline particle agglomeration. This means that under shear stress the crystallites can come into contact [78, 79], as shown in Fig. 6.14.

In glassy CuZr alloys, the hardness increases with copper content [78]. It is
Figure 6.13: True stress-strain curve for 1mm diameter rod of as-cast Cu$_{50}$Zr$_{50}$ loaded in uniaxial compression. To avoid damage to the testing machine, the test was stopped before sample fracture, at a compressive strain of 52%. The inset shows scanning electron microscopy (SEM) images of the sample (a) before testing and (b) after a compressive strain of 52%. Reproduced from [78].

likely that copper-rich nanocrystals, ideally dislocation free, are harder than the zirconium-enriched matrix. In such a case the size and the agglomeration of crystallites can affect the plastic flow. As a consequence, shear bands, in which there has already been some crystalline particles agglomeration can become more resistant to deformation than the neighboring material [78].

We performed nanoindentation on a CuZr metallic glass obtained through the same method explained in section 5.1. However, after cooling the samples we embed Cu nanocrystals in the glassy matrix as shown in Figs. 6.15a) and 6.16a). The indented samples contain nanocrystals of different size. We will call these samples A and B consisting of 547583 and 1096945 atoms respectively. Sample A has dimensions of 105.9 nm × 52.9 nm × 1.6 nm containing 11 small nanocrystals of 3.5 nm × 3.5 nm × 1.6 nm. Sample B’s geometry is 105.9 nm ×105.9nm × 1.6 nm containing 1 nanocrystal of 20
Figure 6.14: The proposed mechanism of shear-induced coalescence of nanocrystallites. In the undeformed material (a) the crystallites are self avoiding. In an operating shear band (b) the relatively hard crystallites can be brought into contact in the matrix of lowered viscosity. Sintering of the crystallites (c) can occur in a limited time, facilitated by the nanometer scale. Reproduced from [78].
nm × 20 nm × 1.6 nm. The indentation is performed following the same
procedure described in section 3.

Our results show that in both samples the shear bands cannot propagate
through the nanocrystals, but are instead pinned by them. A consequence
may be that the presence of the nanocrystals provides a mechanism of strain
hardening and may assist delocalization of the plastic flow around and be-
tween the nanocrystals as shown in Fig. 6.15(c) and Fig. 6.16(c). Though
the nanocrystals in sample A are smaller than the width of the shear bands
and they are pushed into the sample during deformation we cannot clearly
observe agglomeration of the nanocrystals (see Fig. 6.15(b) and c) as re-
ported for experimental uniaxial deformations [78, 79]. In the case of sample
B, the nanocrystal is larger than the width of the shear bands in CuZr. As a
consequence of size, the nanocrystal itself behaves as a small nanoindenter,
and beneath it we can observe activation of shear bands while it is pushed
into the glassy matrix during the deformation process.
Figure 6.15: Nanoindentation on sample A (CuZr glass sample containing 11 fine crystalline particles with a size of 3.5 nm × 3.5 nm × 1.6 nm); a) undeformed sample, b) indented sample with a velocity of 7m/s at maximum depth of 60Å; c) visualization of strain localization under the indenter using $D^2_{\text{min}}$ method described previously.
Figure 6.16: Nanoindentation on sample B (CuZr glass sample containing a crystalline particle with size of 20 nm × 20 nm × 1.6 nm); a) undeformed sample, b) indented sample with a velocity of 7m/s at maximum depth of 60Å; c) visualization of strain localization under the indenter using $D_{min}^2$ method described previously.
Chapter 7

Conclusions

The purpose of this thesis was to model and study the mechanical properties of CuZr and CuMg metallic glasses and potentially to contribute to a better understanding of this properties. With the hope that we have succeed to do that we will conclude now our main results.

A new EMT interatomic potential was constructed for CuZr, with the purpose of simulating CuZr bulk metallic glass. The potential was fitted to lattice constants, cohesive energies and elastic properties of elemental Cu, elemental Zr and Cu_{50}Zr_{50} in the B2 crystal structure. The fitted potential does a reasonable job of reproducing lattice constants and energies of other structures of Cu_{50}Zr_{50}. When a glassy sample of Cu_{50}Zr_{50} is produced, we find the glass transition temperature, elastic constants and structural data in form of average coordination numbers and average nearest neighbor interatomic distances in good agreement with experiment. Previously, an interatomic force field has been fitted to CuZr by Duan et al. 35 but we find that our new EMT interatomic potential described in chapter 4 provides a better description of the structure of the metallic glass.

Using EMT interatomic potential for CuZr, we have investigated shear band formation during homogeneous shear and during nanoindentation in CuZr and MgCu-based metallic glasses. The studied samples are quasi two-dimensional. In homogeneous shear, we observe formation of shear bands of 5 and 8 nm in thickness for CuZr and MgCu-based glasses, respectively.
During nanoindentation, we see a clear signature of shear band formation under the indenter, although the shear bands are not as well developed as in two-dimensional Lennard-Jones simulations [28]. However, a direct comparison is not possible due to the computational costs of the EMT potentials which does not allow us to use the same low velocities and cooling rates.

The shear bands are seen to form gradually during indentation. Shear band formation is stronger if the indentation velocity is low, if the indenter is large and if the sample is cooled slowly. In addition, shear bands were more clearly visible clearer in CuZr than in MgCu under otherwise identical conditions, probably due to the natural width of the shear bands in MgCu being larger. Simulations of nanoindentation in nanocrystalline copper under otherwise identical conditions show a significantly different deformation mechanism, where individual dislocations strongly influence the deformation pattern.

When indenting glassy samples containing nanocrystals we observed that the shear bands cannot propagate through the nanocrystals, being pinned by them. This may lead to a mechanism of hardening.
Bibliography


Simulations of Mechanical Properties of Metallic Glasses


Simulations of Mechanical Properties of Metallic Glasses


[58] N. P. Bailey, (private communication).


An Interatomic Potential for Studying CuZr Bulk Metallic Glasses**

By Anca Păduraru, * Abder Kenoufi, Nicholas P. Bailey and Jacob Schiøtz

Binary alloys capable of forming metallic glasses have been discovered recently.1–8 The mechanical properties of BMGs are remarkably different from the ones of ordinary metallic alloys due to the atomic level disorder in the glassy state. Unlike crystalline materials plastic deformation in metallic glasses cannot be caused by lattice defects but takes place through atomic-scale deformation events and may further involve localization through formation of shear bands. For understanding the origin of their mechanical properties it is important to get the basic understanding of fundamental theoretical problems through atomistic simulations.

Molecular dynamics (MD) treats atomic systems according to Newtonian mechanic laws. Atoms are point particles, interacting through an interatomic potential, describing the energy of an atom as a function of the positions of all atoms in a neighboring region of space. The time evolution of the system is obtained by numerically integrating Newton’s second law. Often the interatomic potential is a classical potential, no quantum mechanical description of the material is attempted, but the functional form of the potential may be derived from quantum mechanical arguments.9 MD is able to treat systems with millions of atoms, and permits the average calculations of transport (diffusion, thermal conductivities, viscosity), or mechanical quantities (elastic constant, plastic yield), and also the modeling of complex phenomena (shear band localization, fracture appearance, neutronic cascades).

The quality of the results will depend on the quality of the interatomic potential, simple potentials giving a less accurate description of the interatomic interactions while allowing very large simulations, more complicated potentials may give a better description of the interaction, but limit the simulation size. Many-body potentials such as the Embedded Atom Method10 and the Effective Medium Theory (EMT)11,12 have been shown to give a good description of the late transition metals crystallizing in close-packed structures, and their alloys, while still allowing simulations with millions of atoms.13 In this paper, we create an EMT potential optimized for modeling the mechanical and thermodynamic properties of CuZr bulk metallic glass.

CuZr was recently discovered to be a binary bulk metallic glass.6,14 Since binary alloys are easier to model than alloys with more elements, this makes CuZr an attractive bulk metallic glass to study theoretically. Previously, an interatomic force field has been fitted to CuZr by Duan et al.,28 but we find that the EMT force field described here provides a better description of the structure of the metallic glass. The potential developed here will be used to model the mechanical properties of CuZr, to be published elsewhere.

Fitting an Effective Medium Theory Potential

The functional form of EMT is described by Jacobsen et al.,[15] and will not be repeated here, as it is rather complex. The energy of each atom is the sum of two terms, the cohesive energy and the atomic-sphere correction. The cohesive energy approximates the energy of an atom with the energy of an atom in a perfect face-centered cubic (FCC) crystal with the same electron density. Each atom contributes to the local electron density in its neighborhood with an exponentially decaying density. Two EMT parameters describe this contribution to the electron density: \( n_0 \) describes its magnitude, and \( n_2 \) is the inverse decay length. The energy of an atom is then a function of the electron density at its positions, this function has a minimum determining the equilibrium lattice constant. The EMT parameters \( n_0 \) and \( E_0 \) describes the position of this minimum, the curvature, and the depth, respectively. The atomic-sphere correction handles departures from the reference FCC structure. It is described as the difference between

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a pair potential in the actual structure and the same pair potential in the reference structure. This pair potential is also an exponentially decaying function, the EMT parameters \( V_0 \) and \( \kappa \) describe the strength and inverse decay length. The atomic-sphere correction term is responsible for a system’s resistance to shear.

EMT does not contain special parameters for describing the interactions between unlike atoms in an alloy, instead these interactions are described by combining the potential parameters for the elements. For example, the cohesive energy of a Cu atom surrounded by Zr atom will depend on the Cu parameter describing how the energy of the Cu atom depends on the local electron density \( (s_0, \lambda, E_0) \), and on the Zr parameter describing how this density decays near the Zr atom \( (n_0, \eta) \).

We fit the seven parameters relating to Zr, while keeping the Cu parameters fixed to the values obtained in a previous work on the CuMg metallic glass.\[15\] We do the fitting by minimizing an error function

\[
 f(\{p\}) = \sum_i q_i \cdot | C_i^{\text{EMT}} (\{p\}) - C_i^{\text{target}} |^2
\]  

(1)

where \( \{p\}=[s_0, n_0, E_0, V_0, \alpha, \lambda, \kappa] \) is the list of parameters that need to be fitted, \( q_i \) are normalizing constants, \( C_i^{\text{EMT}} \) and \( C_i^{\text{target}} \) are the EMT values (obtained from molecular dynamics) and target values (from experiment or from DFT calculations, respectively. The sum goes over the different properties used to fit the potential, such as lattice constants, cohesive energies and elastic constants for Cu, Zr and the CuZr alloy in the B2 (or CsCl) structure, see Table 1.

The target values were obtained from quantum mechanical calculations using Density Functional Theory within the generalized gradient approximation (DFT-GGA), using the Perdew-Wang 91 exchange-correlation functional\[19\] and ultrasoft pseudopotentials. Calculations were performed with the dacapo program from the CAMP Open Software project.\[20\] The usual care was taken to ensure convergence with respect to plane wave cutoff (350 eV), number of k-points \((8 \times 8 \times 8)\) etc.

For fitting the interatomic potential parameters we use a Nelder Mead simplex method\[21\] for optimizing the Function 1 described above. The method requires only evaluations of the functions and not their derivatives for finding the minimum of more than one independent variable.

The result of the fit is shown in Table 1, showing how well the target values were fitted, and Table 2 showing the resulting EMT parameters for Cu and Zr.

### Testing the Potential

Before using the potential obtained in the previous sections, it is important to test its ability to predict properties not used in the fitting procedure. Since the intended application

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( s_0 ) (Å)</td>
<td>1.41</td>
<td>1.78</td>
</tr>
<tr>
<td>( E_0 ) (eV)</td>
<td>-3.51</td>
<td>-6.3</td>
</tr>
<tr>
<td>( \lambda ) (Å(^{-1}))</td>
<td>3.693</td>
<td>2.247</td>
</tr>
<tr>
<td>( \kappa ) (Å(^{-1}))</td>
<td>4.943</td>
<td>3.911</td>
</tr>
<tr>
<td>( V_0 ) (eV)</td>
<td>1.993</td>
<td>2.32</td>
</tr>
<tr>
<td>( n_0 ) (Å(^{-1}))</td>
<td>0.0637</td>
<td>0.031</td>
</tr>
<tr>
<td>( \eta ) (Å(^{-1}))</td>
<td>3.039</td>
<td>2.282</td>
</tr>
</tbody>
</table>

Table 2. EMT parameters.

### Table 3. Comparison between DFT and EMT results for different crystal structures for Cu50Zr50. The B2 structure was used in the fitting of the potential, the other structures are tests of the potential.

<table>
<thead>
<tr>
<th>Structure</th>
<th>E (eV/atom)</th>
<th>V (Å /atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu50Zr50B1</td>
<td>(DFT-GGA)</td>
<td>0.275</td>
</tr>
<tr>
<td>(EMT)</td>
<td>0.203</td>
<td>18.60</td>
</tr>
<tr>
<td>Cu50Zr50B2</td>
<td>(DFT-GGA)</td>
<td>-0.1202</td>
</tr>
<tr>
<td>experiment[17]</td>
<td>-0.14</td>
<td>—</td>
</tr>
<tr>
<td>(EMT)</td>
<td>-0.139</td>
<td>16.38</td>
</tr>
<tr>
<td>Cu50Zr50L10</td>
<td>(DFT-GGA)</td>
<td>-0.035</td>
</tr>
<tr>
<td>(EMT)</td>
<td>-0.0011</td>
<td>17.23</td>
</tr>
<tr>
<td>Cu50Zr50L11</td>
<td>(DFT-GGA)</td>
<td>0.250</td>
</tr>
<tr>
<td>(EMT)</td>
<td>-0.1295</td>
<td>18.25</td>
</tr>
</tbody>
</table>
is CuZr metallic glasses, the potential is both tested on ordered alloys with the same composition, and on thermodynamical and structural properties of the metallic glass.

The first test consists of comparing the formation energies and lattice constants (here expressed as a volume per atom) for four different ordered alloys. These structures do not exist in nature; the B2 (or CsCl) structure is the stable crystal structure for Cu50Zr50. However, the other structures can be set up in the computer, and the energies and lattice constants can be compared to more accurate DFT calculations. The results are given in Table 3. If the potential is able to describe low-energy ordered structures, it is likely to correctly describe the local structures occurring in a metallic glass as well. All the structures except the L11 structure are well described. The L11 structure consists of alternating close-packed layers of Cu and Zr, this structure is presumably far from what one will encounter in metallic glasses, and the inability to reproduce that formation energy is not too worrying.

A more relevant test is to examine how this potential performs when used on a metallic glass. We therefore prepared a CuZr metallic glass in order to compare the glass transition temperature and the short-range order as measured by the radial distribution function to experiment.

We performed MD simulations in order to obtain the CuZr glass phase from the melt. We used two different systems sizes, starting from body-centered cubic crystals with 2048 and 42600 atoms, and the sites randomly occupied by Cu and Zr. The resulting glassy systems were cube-shaped with side lengths of 3.3 nm and 9.1 nm, respectively. The systems were cooled from 1400 K (well above the melt temperature) in steps of 25 K, with an average cooling rate of 0.54 K/ps. Each temperature step begins with a short period of Langevin dynamics[22] to thermalize the system to the new temperature, followed by a simulation with constant (N,P,T) dynamics, using a combination of Nosé-Hoover and Parrinello-Rahman dynamics.[23,24] The prethermalization with Langevin dynamics is necessary to prevent oscillations in the temperature otherwise seen when the temperature of a Nosé-Hoover simulation is changed abruptly. During the constant (N,P,T) dynamics we recorded averages of different quantities of interest like pressure, volume, kinetic and potential energy of the system, in order to perform the thermodynamics analysis.[15] The simulations were performed using the ASAP program from the CAMP Open Software project.[20]

When plotting the enthalpy versus temperature (inset of Fig. 1), we observe a change in the slope near 600–700 K which indicates the glass transition. From this slope the heat capacity vs. temperature (Fig. 1) can be determined. The change in the heat capacity indicates the glass transition, \( T_g \). We extracted the glass transition temperature by taking the centered derivative of \( C_p(T) \) and choosing the maximum.\[15\] \( T_g \) was estimated to be 620 K, compared to the experimental value of 670 K.\[25\] This good agreement is encouraging, in particular when one considers that no data on glasses and no thermodynamical data at all was used to fit the potential.

The radial distribution function analysis (RDF) is a standard method for obtaining information about the structure of the systems, especially for liquids and amorphous structures. In Figure 2 we show partial RDF functions \( g_{Cu-Cu} \), \( g_{Cu-Zr} \), \( g_{Zr-Zr} \) at the glass transition temperature. The first peaks of the RDF indicate the average distance at which we find nearest neighbor atoms, \( g_{Cu-Cu} \) and \( g_{Zr-Zr} \) yields the distance between like atoms, \( g_{Cu-Zr} \) the distance between unlike atoms. By integrating the RDF functions until the first minimum, we obtain the number of nearest neighbors atoms for Cu and Zr atoms. The results are summarized in Table 4 with comparison with other experimental and simulations data. The values for the coordination numbers and the interatomic distances are in good agreement with the experimental ones, although the interatomic distances are slightly underestimated, and the CuZr coordination number is slightly overestimated. The differences are, however, no larger than the differences between the different experiments.

![Fig. 1. Specific heat vs. temperature for two different sizes of CuZr metallic glass system during annealing. Inset: Enthalpy versus temperature for the 2048 atoms system.](image1)

![Fig. 2. Radial distribution function for CuZr metallic glass.](image2)
Table 4. Average nearest neighbor distances and coordination numbers. The first line is this work, the two next are experimental data with two different methods. The last line is simulations by Duan et al. with another potential and a slightly different composition. Since Cu and Zr are present in unequal amounts, the number of Zr neighbors to a Cu atom is different from the number of Cu neighbors to a Zr atom, and two numbers are therefore given for N(CuZr).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Method</th>
<th>CuCu (Å)</th>
<th>CuZr (Å)</th>
<th>ZrZr (Å)</th>
<th>N Cu</th>
<th>N Zr</th>
<th>N ZrZr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu50Zr50</td>
<td>This work</td>
<td>2.56</td>
<td>2.75</td>
<td>3.13</td>
<td>4.44</td>
<td>6.24</td>
<td>7.59</td>
</tr>
<tr>
<td>Cu50Zr50</td>
<td>EXAFS</td>
<td>2.57</td>
<td>2.84</td>
<td>3.19</td>
<td>4.1</td>
<td>5.4</td>
<td>7.4</td>
</tr>
<tr>
<td>Cu50Zr50</td>
<td>XRD</td>
<td>2.68</td>
<td>2.80</td>
<td>3.16</td>
<td>4.6</td>
<td>4.8</td>
<td>7.8</td>
</tr>
<tr>
<td>Cu46Zr54</td>
<td>Simul.</td>
<td>2.67</td>
<td>2.78</td>
<td>3.22</td>
<td>3.2</td>
<td>7.6/7.5</td>
<td>9.1</td>
</tr>
</tbody>
</table>

As a final test, we have compared the bulk and shear modulus with experimental values. Our calculated values were obtained at zero temperature by applying strain in the elastic limit and relaxing the structure each strain step. We find 108.69 GPa and 29.25 GPa, respectively, compared to the experimental values 101.2 GPa and 31.3 GPa. The deviation is less than 8 %.

Conclusion
An EMT interatomic potential was fitted for CuZr, with the purpose of simulating the CuZr bulk metallic glass. The potential was fitted to lattice constants, cohesive energies and elastic properties of elemental Cu, elemental Zr and Cu50Zr50 in the B2 crystal structure. The fitted potential does a reasonable job of reproducing lattice constants and energies of other structures of Cu50Zr50, when a glassy sample of Cu50Zr50 is produced, we find a glass transition temperature, elastic constants and structural data in form of average coordination numbers and average nearest neighbor interatomic distances in good agreement with experiment.

Paper II
Computer simulations of nanoindentation in Mg-Cu and Cu-Zr metallic glasses

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The formation of shear bands during plastic deformation of Cu$_{6.5}$Zr$_{0.5}$ and Mg$_{0.85}$Cu$_{0.15}$ metallic glasses are studied using atomic-scale computer simulations. The atomic interactions are described using realistic many-body potentials within the Effective Medium Theory. The metallic glasses are deformed both in simple shear and in a simulated nanoindentation experiment. Plastic shear localizes into shear bands with a width of approximately 5 nm in CuZr and 8 nm in MgCu. In simple shear, the shear band formation is very clear, whereas only incipient shear bands are seen in nanoindentation. The shear band formation during nanoindentation is sensitive to the indentation velocity, indenter radius, and the cooling rate during the formation of the metallic glass. For comparison, a similar nanoindentation simulation was made with a nanocrystalline sample, showing how the presence of a polycrystalline structure leads to a different and more spatially distributed deformation pattern, where dislocation avalanches play an important role.

PACS numbers: 62.20.F-, 61.43.Dq

I. INTRODUCTION

Since the discovery of metallic glasses, there has been a great interest in understanding and improving their mechanical properties. The main obstacle for applications of bulk metallic glasses is their brittleness, due to intense localization of the plastic deformation into shear bands. This localization is presumably due to the lack of work hardening in amorphous alloys. This difference between the macroscopic mechanical behavior of amorphous and crystalline alloys is caused by the fundamentally different atomic-scale deformation mechanisms of the two classes of materials. In crystalline alloys, plastic deformation is carried by dislocations, which multiply and eventually entangle in a deforming crystal, leading to work hardening. In an amorphous alloy, dislocations are not possible due to the lack of a crystal structure, and deformation proceeds through localized deformation events. Since these events do not lead to local strengthening, deformation may localize into shear bands.

For these reasons, much work has been done to study deformation and shear band formation in metallic glasses with atomic-scale simulation methods. Most of this work has been done with Lennard-Jones model systems, sometimes in two dimensions to make the system sizes larger for the same computational burden. While Lennard-Jones systems can capture much of the essential physics of a deforming metallic glass, the description of the atomic interactions is too simple to give a realistic description of a specific metallic glass. For such a purpose, many-body potentials such as the Embedded Atom Method or the Effective Medium Theory (EMT) recently fitted to describe these materials. Samples of metallic glass were produced by cooling the systems from 1400K (well above the melting temperature) to the final temperature in steps of 25K, with an average cooling rate of 0.54K/ps, following the procedure published previously. In all cases periodic boundary conditions were used along all three axes during the cooling procedure, for the subsequent deformation simulations the periodicity along one axis was later removed.

Samples with two sizes were made. Small samples containing 62 400 atoms were produced to be used for simple shear deformation. The sample dimensions were 52.9 nm × 12.2 nm × 1.6 nm for CuZr and 57.0 nm × 13.1 nm × 1.7 nm for MgCu. These samples were cooled to 50 K.

Much larger samples were needed for the nanoindentation simulations: Samples were created with dimensions

II. CREATING VIRTUAL METAL GLASS SAMPLES

We perform quasi-two-dimensional molecular dynamics simulations on binary alloys in order to simulate nano-indentation. The materials are Cu$_{6.5}$Zr$_{0.5}$ and Mg$_{0.85}$Cu$_{0.15}$, described with EMT potentials recently fitted to describe these materials. Samples of metallic glass were produced by cooling the systems from 1400K (well above the melting temperature) to the final temperature in steps of 25K, with an average cooling rate of 0.54K/ps, following the procedure published previously. In all cases periodic boundary conditions were used along all three axes during the cooling procedure, for the subsequent deformation simulations the periodicity along one axis was later removed.

Samples with two sizes were made. Small samples containing 62 400 atoms were produced to be used for simple shear deformation. The sample dimensions were 52.9 nm × 12.2 nm × 1.6 nm for CuZr and 57.0 nm × 13.1 nm × 1.7 nm for MgCu. These samples were cooled to 50 K.

Much larger samples were needed for the nanoindentation simulations: Samples were created with dimensions
of 52.9 nm × 52.9 nm × 1.6 nm for CuZr and 57.2 nm × 57.2 nm × 1.7 nm for MgCu, both corresponding to 270 000 atoms. These samples were cooled to 116 K. Before nanoindentation, the samples were replicated in the x direction, giving, e.g., a CuZr sample size of 105.9 nm × 52.9 nm × 1.6 nm, with periodic boundary conditions along the x and z directions, and free boundaries in the y direction.

III. DEFORMATION IN SIMPLE SHEAR

We deformed the metallic glasses under simple shear, using a geometry illustrated in Fig. 1. The sample is divided into three parts, two outer “walls” of 3 nm thickness, and a central part. In the central part, the dynamics of the atoms is left unperturbed, but in the two walls the center of mass motion is constrained, so the two walls move with a constant relative speed. The atoms in the walls are not held rigid; they can still move with respect to each other, since only the mass-weighted sum of their velocities is held fixed. By causing one wall to move in the y-direction, a shear deformation with constant shear rate is applied to the system. The system has periodic boundary conditions in the y and z directions, but free boundaries in the x direction. The shear simulations are done at a temperature of 50 K.

During the deformation, velocity profiles (average atomic velocities as a function of x-coordinate) are calculated. Both velocity profiles and plots of the deformed system clearly show the formation of shear bands (see Fig. 2). Visual inspection indicates that the width of the shear bands is 5 nm for the CuZr glass, and almost 10 nm for the MgCu glass; the latter is consistent with the simulations of Bailey et al.\textsuperscript{15} A better estimate can be obtained by fitting the velocity profiles to a Fermi function \( \frac{1}{\exp(x/\alpha) + 1} \) or to the arctan\((x/\alpha)\) function, the former gives a slightly better fit as the tails of the arctan function are too large. This gives a width parameter \( \alpha \) of 1.51 nm for CuZr and 1.93 nm for CuMg, corresponding to shear band widths of 6 and 8 nm, respectively, as the majority of the variation of the Fermi function occurs in the interval from \(-2\alpha\) to \(2\alpha\). The fits to the arctan function give \( \alpha = 1.23 \) nm and 2.03 nm corresponding to shear band widths of 5 and 8 nm for CuZr and CuMg. In all cases the fits were done with four free parameters: the width, an amplitude and two translations.

IV. NANOINDENTATION

To simulate nanoindentation, we perform molecular dynamics using Langevin dynamics\textsuperscript{24} at a constant temperature of 116 K. During the simulation, an indenter is pushed into the sample at constant velocity. Since the samples are very thin in the z direction, the simulation is quasi two-dimensional, and we choose to use a cylindrical indenter (see Fig. 3). The indenter is modeled as a repulsive potential, as proposed by Shi and Falk.\textsuperscript{25} The form of the repulsive potential is

\[
E = c (r_{xy} - R)^{-6}
\]

where \( r_{xy} \) is the distance in the x-y plane from the center of the indenter to the atom, and \( R \) the indenter radius. The strength parameter \( c = 2.0 \text{ eV Å}^6 \). The indenter is lowered into the substrate under displacement control recording at each step the load and the total displacement. During indentation, the lower edge of the system is held fixed by fixing the positions of the atoms in the

FIG. 1: The setup used for simple shear deformations. The shear is applied by forcing the walls to move as indicated by the arrows. There are periodic boundary conditions in the y and z directions.

FIG. 2: Shear deformation on CuZr and MgCu thin sample and velocity profile with respect to the length. The width of the shear bands were found to be 5–6 nm for CuZr and 8 nm for MgCu.

\[\text{\textsuperscript{}}\]
FIG. 3: The geometry used during nanoindentation. The cylindrical indenter is modeled as a repulsive potential. There are periodic boundary conditions in the $x$ and $y$ directions (left-right and out of the plane of the paper). The upper surface is free, the lower surface is held fixed by fixing the positions of all atoms in a 0.8 nm thick layer.

To visualize the plastic flow and the localization of the shear bands we use the $D_{\text{min}}^2$ method introduced by Falk and Langer. $D_{\text{min}}^2$ quantifies the local deviation from affine deformation during the interval of time between a pair of configurations.

A. Formation of shear bands under the nanoindenter

A nanoindentation simulation is performed on the CuZr sample as described above. The cylindrical indenter with a radius of 30 nm is indented into the sample with a velocity of 7 m/s, as illustrated in Fig. 3. As the shear is inhomogeneous, it is not possible to rigorously define an equivalent shear rate, but it corresponds roughly to a shear rate of the order of $10^8 \text{s}^{-1}$ (a homogeneous shear rate of $10^8 \text{s}^{-1}$ would correspond to the ends of the sample moving with a relative velocity of 10 m/s).

During nanoindentation, the net force on the indenter is recorded as a function of indentation depth, see Fig. 4. The curve is not smooth, but contains small serrations, presumably reflecting individual events during deformation. It would be tempting to interpret this as the formation of individual shear bands, but that interpretation is not supported by direct visualization of the shear band formation. As it is seen in Fig. 4, the shear bands are not formed at once, but grow gradually during the nanoindentation. Just like in the simulations of Shi and Falk, the curved shape of the emerging shear bands corresponds to the expected directions of the maximally resolved shear stress, as predicted by slip line theory.

The shear bands are less clearly formed than in the simulations of Shi and Falk. The simulations cannot, however, be directly compared as the simulations of Falk and Shi are two dimensional and use a Lennard-Jones model potential, whereas our simulations have a finite (but small) thickness, and use a more realistic (but also complex) potential. The more complicated potential combined with the larger number of atoms due to the
finite thickness leads to a much larger computation burden, and our indentations are therefore necessarily done with higher indentation velocities. There are thus three major differences between these simulations and the simulations by Shi and Falk: the dimensionality, the potential and the indentation speed, and it is not surprising that the results are somewhat different.

B. Influences on the shear band formation.

In this section we study how the shear band formation is influenced by varying the parameters of the nanindentation, corresponding to varying physical parameters during a nanindentation experiment. We vary the indenter velocity, its radius, the cooling rate during glass formation and the composition of the glass. All modifications are relative to a “standard simulation” of a CuZr metallic glass produced at a cooling rate of 0.44 K/ps, indented with a cylindrical indenter with radius 30 nm and indentation velocity 7 m/s.

Fig. 5 shows how the shear band formation is influenced by the indentation velocity. A simulation with indentation velocity of 30 m/s is compared with the reference simulation. The shear band formation is less obvious in the fast indentation. A clear indentation rate dependence of the load displacement curve is also seen; the loading force — and thus the stress in the material — is significantly higher during the fast simulation, but no qualitative differences are seen. It can be speculated that even lower indentation rates will lead to formation of fewer and larger shear bands, and possibly lead to macroscopic failure through a few very large shear bands.

Despite the indenter diameter being an order of magnitude larger than the width of the shear band, a difference is also seen when the indenter radius is varied. This is illustrated in Fig. 6, where the effect of reducing the indenter radius by 33% is studied. As is seen, fewer shear bands are formed, when we have chosen to compare situations with the same indentation depth. It is likely that this difference is at least partly caused by less material being displaced by the smaller indenter.

The effect of changing the cooling rate during the glass formation is investigated in Fig. 7, where identical nanoindentation simulations are performed on two samples produced with cooling rates of 2.2 K/ps and 0.44 K/ps. In this case the difference is less pronounced, but the shear band appears more distinct in the slowly cooled sample. This is consistent with results by Shi and Falk showing a stronger tendency for shear localization for slowly annealed systems.

Finally, we investigated the consequences of replacing the CuZr glass with a MgCu glass (Fig. 8). Shear localization is far more pronounced in the CuZr sample. This is consistent with our previous findings that shear bands are approximately twice as wide in MgCu glass (see also Fig. 2.

V. NANOINDENTATION OF NANOCRYSTALLINE SAMPLES

For comparison, we subjected a nanocrystalline sample to indentation in a similar manner. Nanoindentation of nanocrystalline samples has previously been studied by Van Swygenhoven et al., with a particular fo-
FIG. 8: Comparison of MgCu (a) and CuZr metallic glass under otherwise identical nanoindentation conditions. The latter shows the strongest shear localization.

cus on the onset of plastic deformation under a spherical indenter. In this work we have chosen to mimic the indentation parameters used for the metallic glass, so the nanocrystalline sample is quasi-twodimensional with ⟨110⟩-directions along the thin direction (the z direction). This orientation is chosen to maximize the number of possible slip systems in the crystal, which is nevertheless still significantly lower than in a full three-dimensional simulation. The material for this simulation is copper, described with the EMT potential.

The nanocrystalline sample was made by a random Voronoi construction. Random grain centers were chosen, and the part of space closer to a given grain center than to any other grain center was filled with a randomly rotated crystal, as published previously.

The sample has the same dimensions as the CuZr metallic glass sample, and similarly to the glassy sample, it is made by repeating a system with half the size in the x direction. The average grain diameter is 15 nm. The annealing is, however, only done from a temperature of 464 K (kT = 0.04 eV), staying well below the melting point to preserve the nanocrystalline structure. The indentation is done to a depth of around 5 nm, comparable to the simulations with metallic glass. After the simulation, the local atomic structure is analyzed with the Common Neighbor Analysis, identifying atoms which are locally coordinated as face-centered cubic (grain interiors), hexagonal closed-packed (stacking faults and twin boundaries) or otherwise (grain boundaries and dislocation cores).

Figure 9 shows the deformation during this nanoindentation, and Fig. 10 the corresponding load displacement curves. A number of noteworthy features are marked by letters on Fig. 9b.

Right below the indenter (marked “A”), the plastic deformation is severe, and several grain boundaries have disappeared. These are low-angle grain boundaries, which can be regarded as dense arrays of dislocations. The high stress below the indenter causes these to move. Many stacking faults are seen; they are caused by the high stress levels, making the energy of the stacking fault irrelevant compared to the elastic energy. Another example of a low angle grain boundary disappearing as a result of dislocation migration is marked “B”.

A few grain boundaries “reconstruct” under the applied stress by emitting an array of partial dislocations (for example at “C”). Presumably a lower grain boundary energy can be obtained and some of the applied stress relieved by the motion of the dislocation wall, at the expense of creating some stacking faults. A similar phenomenon is seen at “D”, where a wall of full dislocations has been emitted by the grain boundary, and an extreme case at “E”, where a grain boundary has split into two

FIG. 9: Nanoindentation of nanocrystalline copper. (a) The initial configuration before indentation. Atoms in the grain interiors are not shown, atoms at stacking faults and twin boundaries are colored red, atoms in grain boundaries, dislocation cores and at surfaces are blue. Both high-angle and low-angle grain boundaries are seen, the former are shown as blue walls, the latter are seen to be made of individual dislocations, for example the one marked “1”. A few stacking faults created by dislocation activity during annealing are also seen. (b) After nanoindentation, significant plastic deformation has occurred, in particular just under the indenter, where numerous stacking faults and deformation twins have appeared. The letters A – F mark features discussed in the text. (c) A deformation map shows that the majority of the deformation occurs inside the grains and is caused by dislocation activity, although some grain boundary sliding is also seen.
separated by a region of (slightly faulted) HCP crystal. Similar reconstructions of grain boundaries under stress have previously been seen in computer simulations. At “F” a stacking fault has been removed by the motion of a partial dislocation, and a new one has been created nearby by an independent event, creating the illusion that a stacking fault has moved.

The events discussed above can also be found in the displacement map in Fig. 9c. The figure shows a striking difference between the deformation distributions in the glass and in the nanocrystalline sample: in the crystalline sample the spatial distribution of the deformation is much more uneven, as it is controlled by the polycrystalline structure. Deformation can only occur at grain boundaries, or where dislocations are available, typically from grain boundary sources.

The load-displacement curve in Fig. 10 shows significantly larger serrations than for the glassy samples. This is caused by avalanches of dislocation activity. The insets show how the deformation occurs just before and during one of the serrations, it is clearly seen that the serration does not correspond to a single dislocation event, but rather to an avalanche of events.

VI. SUMMARY AND CONCLUSION

We have investigated shear band formation during homogeneous shear and during nanoindentation in CuZr- and MgCu-based metallic glasses, using realistic interatomic potentials within the Effective Medium Theory. In homogeneous shear, shear bands of 5 and 8 nm thickness form in the CuZr- and MgCu-based glasses, respectively. In nanoindentation, we see a clear signature of shear band formation under the indenter, although the shear bands are not as well developed as in two-dimensional Lennard-Jones simulations. The shear bands form gradually during indentation. Shear band formation is stronger if the indentation velocity is low, if the indenter is large and if the sample was cooled slowly. In addition, shear bands were clearer in CuZr than in MgCu under otherwise identical conditions, probably due to the natural width of the shear bands in MgCu being larger.

Simulations of nanoindentation in nanocrystalline copper under otherwise identical conditions show a significantly different deformation mechanism, where individual dislocations strongly influence the deformation pattern.

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