MOLECULAR DYNAMICS SIMULATIONS OF STRUCTURE-PROPERTY RELATIONSHIPS IN CU–ZR METALLIC GLASSES


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GLASSES

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On the cover: Defective icosahedral network in a shear band in an amorphous Cu$_{64}$Zr$_{36}$ nanowire.
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<td>BMG</td>
<td>bulk metallic glass</td>
</tr>
<tr>
<td>CSRO</td>
<td>chemical short range order</td>
</tr>
<tr>
<td>EAM</td>
<td>embedded atom method</td>
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<tr>
<td>EXAFS</td>
<td>extended x-ray absorption fine structure</td>
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<tr>
<td>fcc</td>
<td>face centered cubic</td>
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<td>FI</td>
<td>Cu-centered full icosahedron</td>
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<td>FS</td>
<td>Finnis-Sinclair</td>
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<tr>
<td>hcp</td>
<td>hexagonal close packed</td>
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<td>MD</td>
<td>molecular dynamics</td>
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<td>MG</td>
<td>metallic glass</td>
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<td>MRO</td>
<td>medium range order</td>
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<tr>
<td>MSD</td>
<td>mean square displacement</td>
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<td>NBED</td>
<td>nanobeam electron diffraction</td>
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<td>NG</td>
<td>nanoglass</td>
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<td>NN</td>
<td>nearest neighbor</td>
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<td>OSP</td>
<td>original site peak</td>
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<td>PEL</td>
<td>potential energy landscape</td>
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<tr>
<td>PRDF</td>
<td>partial radial distribution function</td>
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<tr>
<td>RDF</td>
<td>radial distribution function</td>
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<tr>
<td>RMC</td>
<td>reverse Monte Carlo</td>
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<tr>
<td>SB</td>
<td>shear band</td>
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<tr>
<td>SCL</td>
<td>supercooled liquid</td>
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<td>SRO</td>
<td>short range order</td>
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<tr>
<td>ST</td>
<td>shear transformation</td>
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<tr>
<td>STZ</td>
<td>shear transformation zone</td>
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<td>TSRO</td>
<td>topological short range order</td>
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<tr>
<td>VP</td>
<td>Voronoi polyhedron</td>
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<td>XRD</td>
<td>x-ray diffraction</td>
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ABSTRACT

Metallic glasses have been the subject of intense research in the past 50 years and especially since the 1990s, after the discovery of the first bulk metallic glasses \cite{1,2,3}, the scientific interest in this class of materials has been rapidly increasing. One of the enduring attractions of metallic glasses are their unique mechanical properties. Metallic glasses exhibit elastic moduli on the same order as conventional engineering materials and room temperature strengths significantly in excess of polycrystals with similar composition \cite{4,5}. However, their strong tendency towards shear localization, which results in macroscopically brittle failure at room temperature, has imposed a barrier to broad commercial application \cite{6}. Exploiting the interesting properties of metallic glasses for structural applications requires the development of effective strategies to control strain localization and prevent brittle failure. This can only be realized if the atomic scale mechanisms governing plasticity in metallic glasses are fully understood.

The scope of this thesis is to elucidate structure-property relationships in copper-zirconium amorphous alloys using molecular dynamics simulations. The Cu-Zr system was chosen as it is one of the few binary alloy systems where metallic glasses can be prepared in a wide composition range from 10 to 80\% Cu \cite{7}, typically by melt-quenching techniques such as melt-spinning or copper mold casting. The main benefit of a binary metallic glass is that the atomic level structure is less complex as compared to a multi-element bulk metallic glass with typically more than three constituting elements \cite{8}, which simplifies the identification of fundamental structure-property relationships. Moreover, suitable interatomic potentials for MD simulations are readily available.

We investigate the plastic deformation of Cu–Zr glasses in the absence of free surfaces or other heterogeneities and show that strain localization is an intrinsic metallic glass property. Tensile tests of metallic glass nanowires reveal that even in samples with a diameter of only 5 nm shear banding is the dominant deformation mode and that there is no intrinsic size effect in the plastic deformation of metallic glasses. The structure and properties of shear bands are investigated in a comprehensive study considering chemical short range order, topological short range order and medium range order. Our results suggest that the picture of a structural backbone, which is locally destabilized and causes strain localization, is not a universal concept for describing shear banding in metallic glasses. When subjected to thermal annealing, shear bands recover and, depending on the annealing temperature, collective motion or nearest neighbor jumps in addition to collective motion are the relevant relaxation mechanisms. Linking free volume theory and experimental observations, our results provide an explanation why
shear bands do not recover instantaneously at elevated temperatures but rather on time scales in the range of hours. We finally investigate the deformation of nanostructured metallic glasses, namely nanoglasses obtained by powder consolidation. Nanoglasses comprise a network of glass-glass interfaces with a defective short range order, which act as shear band precursors. This leads to a more homogeneous distribution of plastic strain in a pattern of multiple shear bands, wherefore we predict an enhanced ductility for metallic nanoglasses as compared to conventional metallic glasses.
Part I

INTRODUCTION
METALLIC GLASSES

The synthesis of an amorphous metal was first reported in 1960 by Klement, Willens and Duwetz, who succeeded to quench a molten Au$_4$Si alloy to an amorphous structure [9]. High critical cooling rates on the order of $10^6$ Ks$^{-1}$ were necessary to quench this alloy into the glassy state. This, however, strongly limited the sample dimensions and only thin amorphous films could be obtained. The main goal of early research on metallic glasses (MGs) was, therefore, to find novel alloy systems with enhanced glass forming abilities and lower critical cooling rates, for facilitating the fabrication of bulk samples. Apart from several promising results with compositions comprising rather exotic elements [10], most technologically relevant bulk metallic glass (BMG) forming alloys* have only been discovered since the late 1980s [1, 2, 3, 11, 12].

While the expression glass was historically reserved for amorphous solids synthesized by melt-quenching, the term amorphous solid generally applies to any solid having a non-periodic atomic structure [13]. Since all samples studied in this thesis are prepared by quenching a metallic liquid, the terms amorphous alloy and metallic glass will be used interchangeably.

1.1 THE FORMATION OF AMORPHOUS SOLIDS

1.1.1 The glass transition

In general, a glass is formed when a liquid is quenched into the solid state while crystal formation is kinetically suppressed. A liquid that passes its thermodynamic melting point $T_m$ without crystallization is called supercooled liquid (SCL). The properties of a SCL differ significantly from regular liquids and with decreasing temperature the dynamics of a system can slow by more than 10 orders of magnitude within only a few Kelvin [14]. These dynamics can be expressed by the viscosity $\eta$, which increases dramatically during cooling. An increase in viscosity inhibits atomic rearrangements in the SCL which are necessary to find the equili-

* Conventionally, BMG-formers are defined as alloys that can be cast into a fully amorphous solid whose smallest dimension is 1 mm.
brium volume at the corresponding temperature. If the temperature is so low that atoms cannot sufficiently rearrange on experimental time scales (before the temperature is further lowered), the volume of the system starts to deviate from metastable equilibrium, which is specified by the equilibrium liquid at a given temperature (see Fig. 1; the dashed red line represents the equilibrium liquid). When the temperature is further decreased the system freezes and a glass is formed. The temperature, at which the viscosity takes a value of $10^{12}$ Pa·s is conventionally defined as the glass transition temperature $T_g$ [15]. A viscosity of $10^{12}$ Pa·s corresponds to a time constant for structural relaxations in the range of 1 hour and marks the crossing of an experimental time scale and the time scale for structural relaxations. According to this definition, the glass transition is a kinetic event rather than a thermodynamic transition [14]. The experimental time scale is set by the applied cooling rate and, therefore, $T_g$ changes depending on how fast a system is quenched. If the cooling rate is faster, the atoms will have less time to rearrange and the deviation from the equilibrium liquid will occur at higher temperatures. Comparing the range of experimentally accessible cooling rates, deviations in $T_g$ can be on the order of 10-20% [7].

A phase transition is defined to be second order if it is continuous in volume and enthalpy and if the second order derivatives of the Gibbs function show a discontinuity [13]. Given this definition, the glass transition exhibits certain similarities: While enthalpy $H(T)$ and volume $V(T)$ are continuous, a change in slope occurs at the glass transition, which corresponds to rounded discontinuities in the specific heat $C_p(T)$ as well as in the thermal expansion coefficient $\alpha(T)$ [16]. Yet, the classification of the glass transition as a thermodynamic phase transition certainly contradicts the variation of $T_g$ with cooling rate. Moreover, the features in $H(T)$, $V(T)$, $C_p(T)$, and $\alpha(T)$ are not sharp, and the glass transition occurs over a range of temperatures rather than at a defined temperature [13, 17].

1.1.2 Free volume model

One of the widely recognized models for describing the liquid-glass transition is the free-volume model by Turnbull and Cohen [17, 18, 19]. They developed
1.1 The Formation of Amorphous Solids

a simple theory which accounts for diffusive transport in liquids and glasses and predicts the rapid decrease in atomic mobilities as the glass transition is approached. According to their model, the glass transition results from the decrease of the free volume of the amorphous phase below a critical value. The free volume model is based on two fundamental assumptions: (i) Atomic transport occurs only when voids having a volume greater than some critical value form by the redistribution of free volume. (ii) No energy is required for the redistribution of free volume. In this approach the glass transition can be explained by the temperature dependence of the free volume in a system, which is related to the thermal expansion. When a glass is heated, thermal expansion leads to an increase in volume, but at lower temperature the excess volume is no free volume. Close to the glass transition, however, free volume begins to appear and the viscosity of the system decreases rapidly, leading to liquid-like behavior.

1.1.3 Potential energy landscape and structural relaxations

As discussed above, an as-prepared glass is thermodynamically unstable since it deviates not only from the crystalline state, but also from the equilibrium liquid representing the metastable equilibrium at a given temperature. When a glass is annealed at a temperature near or below the glass transition, structural relaxations occur which lead to an increase in the configurational order of the system: namely relaxation of structure, volume and entropy \[20\]. Such relaxations are associated with significant changes in physical properties like severe embrittlement, and the relaxations can also affect the elastic properties of a glass. As structural relaxations are irreversible processes involving the production of entropy \[21\], the initial glass structure before annealing can only be recovered by annealing in the supercooled liquid regime.

A useful concept to describe structural configurations and relaxations is the potential energy landscape (PEL) \[22, 23\]. An example of a one dimensional PEL is drawn in Fig. 2, where the potential energy is plotted versus all configurational coordinates. Possible structural configurations are local minima in the PEL and when a liquid undergoes a glass transition, the system is trapped into a local minimum of a megabasin. The PEL has a hierarchical structure of megabasins separated by large energy barriers and subbasins separated by small barriers (enlarged section in Fig. 2). Consequently, relaxation mechanisms in glasses are governed by two kinetic processes: (i) the fast and reversible $\beta$-transitions as first reported by Johari and Goldstein \[24\], which involve stochastically activated hopping events across subbasins confined within a megabasin (i.e., intrabasin hopping), and (ii) the slow $\alpha$-transitions involving irreversible hopping events spanning across different megabasins (i.e., interbasin hopping) \[25\]. While $\beta$-relaxations imply only the local rearrangement of a small number of atoms, $\alpha$-relaxations require a global rearrangement of atoms.
METALLIC GLASSES

Figure 2: Schematic of a 1-dimensional potential energy landscape. When zooming into the PEL as shown in the inset, its hierarchical structure of sub- and megabasins appears.

1.1.4 Atomic-level structure

Due to the variety of possible structural configurations amorphous systems can adopt, one of the long-standing questions in the field of metallic glass research is their atomic structure. Other than in the case of crystalline metals where the atomic arrangement is strictly periodic, metallic glasses have no long-range translational or orientational order. Theoretical models [26, 27, 28, 29] and simulation results [30, 31, 32], however, predict a significant degree of short range order (SRO) and even medium range order (MRO), which is supported by recent experimental findings [29, 33, 34, 35, 36]. In this context, SRO denotes a local unit involving nearest neighbor atoms which is characteristic for the structure of a specific amorphous alloy; MRO defines the next level of structural organization and classifies how the SRO-units are clustered to fill space. In the absence of a crystalline lattice, where dislocations with distinct Burgers vectors are the carriers of plastic deformation, it is the short- and medium range order that is expected to control plastic deformation in glasses [37].

General aspects

The first model, which has been widely applied to describe the structure of metallic glasses, is the dense random packing model by Bernal [26]. His model is purely based on the spatial arrangement of hard spheres according to the ratio of their atomic radii and neglects any chemical effects on atomic packing. Despite its relative simplicity, the dense random packing model provides a reasonable description of monoatomic glasses and glasses where the atomic radii of the constituents are comparable [38]. This, however, is not the case
for most technologically relevant metallic glasses, which often contain atoms with significant size differences, apart from the fact that BMG-formers typically comprise more than 3-5 species. Moreover, chemical short range order (CSRO), which is observed for different metallic glasses [39, 40, 33], cannot be described with Bernal’s model. An alternative model was introduced by Gaskell [27], who assumed that the local atomic arrangement in amorphous alloys closely resembles structures and compositions found in corresponding crystalline phases. This stereochemically designed model shows reasonable agreement with neutron scattering data for metal-metalloid-glasses. For the case of metal-metal-glasses, however, the applicability of the model was not confirmed [38]. Another idea for the SRO in metallic glasses arises from the fact that glasses are in principle frozen liquids and, therefore, the atomic structure should be closely related to the structure of the respective SCL. In order to explain the stability of liquids below the thermodynamic melting temperature, Frank [41] suggested that the

Figure 3: Efficient packing of solute-centered clusters in several binary BMGs by icosahedral fivetfold packing [29]. (Reprint by permission from Macmillan Publishers Ltd: Nature 439, 419 (2006); © 2006.)
atoms form icosahedral clusters. Icosahedral packing provides high packing
density and, due to its characteristic five-fold symmetry and the resulting lack in
translational periodicity, requires substantial atomic rearrangements to transform
into crystalline phases in addition to high transformation barriers. According to
Frank’s hypothesis, icosahedral clusters should be present in metallic glasses and
in fact, recent simulations \cite{30, 31, 32} and experimental results \cite{34, 35} confirm
a high fraction of icosahedral atomic clusters in some amorphous alloys. In
contrast, other experimental results \cite{29, 33} report a large variety of different
atomic clusters and no indication for a dominant icosahedral SRO. In light of
this, Sheng \textit{et al.} \cite{29} concluded that the local arrangement in metallic glasses
cannot be modeled by just one stereotype structure like icosahedral clusters.
Instead, metallic glasses are built from a number of differently coordinated atomic
clusters. Yet, their results also show that depending on the alloy system specific
coordination polyhedra occur with high frequency. They identified these special
clusters as Kasper polyhedra \cite{42} and claim that the Kasper polyhedron SRO is
the main underlying topological SRO in metallic glasses.

In order to fully characterize the structure of an amorphous solid, the mere
knowledge of SRO is not sufficient. Other than in the case of crystalline solids,
where the symmetric packing of periodic unit cells links the atomic to the macro-
scopic scale, the rules for packing SRO clusters to end up with a dense glass
sample are less obvious. One concept to model the MRO in metallic glasses
is the efficient cluster packing model proposed by Miracle \cite{28}. He suggests
that solute-centered quasi-equivalent clusters are the local structural motif in
solute lean metallic glasses. An extended structure is obtained by packing the
solute centered clusters in face centered cubic (fcc) or hexagonal close packed
(hcp) configurations to efficiently fill space. The MRO extends to a few cluster
diameters (\(\approx 1\) nm), when the order breaks down due to internal strains and
packing frustration. A similar scheme was introduced by Sheng \textit{et al.} \cite{29}, whose
experimental and simulation results for different binary metallic glasses indicated
that an icosahedral fivefold packing of solute centered clusters is more realistic
than the fcc- or hcp-stacking proposed by Miracle (see Fig. 3). Yet, the dense
packing of single-solute-centered clusters can only describe the structure of alloys
with a low solute concentration. When the concentration of solute atoms increases
above the limit where all solute atoms can be placed in a single-solute-centered
cluster surrounded only by solvent atoms (\(\approx 20\%\)), neighbor contact between
solute atoms will occur. This leads to the formation of strings or even networks
of solute atoms in solute rich alloys, which constitute different types of MRO \cite{29}.

Until recently, the validation of theoretical models for SRO and MRO in metal-
llic glasses was limited to molecular dynamics (MD) simulations \cite{30, 31} and
diffraction techniques in combination with reverse Monte Carlo (RMC) model-
ing \cite{29, 33, 34, 35}. Both approaches, however, implicate certain disadvantages:
RMC modeling involves the fitting of a model glass structure to experimental data† by rearranging atomic positions to minimize the fitting residual. Different structural models, however, can show similarly good agreement with experimental data which is why structural information obtained by RMC is ambiguous. In molecular dynamics simulations on the other hand, glass structures are prepared by melt-quenching using cooling rates which are several orders of magnitude higher than in experiment. One can, therefore, argue that the atomic level structure of metallic glasses simulated with MD and real metallic glasses must not necessarily coincide. Then again, if a significant degree of SRO and MRO are detected in simulated metallic glasses, an even more pronounced structural order can be expected for glasses which are synthesized with lower cooling rates [35]. The first direct evidence for local atomic order in a metallic glass has only been published in 2011 by Hirata and co-workers [36]: Using nanobeam electron diffraction (NBED) they observed well defined diffraction patterns from sub-nanometer regions which are similar to simulated diffraction patterns of individual atomic clusters and their assemblies. Comparing the NBED data with simulations, their results provide direct evidence for atomic order in metallic glasses and confirms theoretical predictions of SRO and MRO.

*Cu–Zr amorphous alloys*

Since Cu–Zr is the alloy system studied in this thesis, the following paragraph provides a more detailed description of what is known about the structure of Cu\(_x\)Zr\(_{1-x}\)-glasses. The common topological feature of SRO in amorphous Cu–Zr is the dominance of Cu-centered icosahedral clusters as suggested by simulation [31, 32, 44] and experimental results [35]. Full-icosahedral (FI) atomic arrangements were found to be locally preferred structures with outstanding properties such as high packing density [45], low configurational enthalpy and entropy [32], high shear resistance [31], and lower atomic mobilities [31]. The degree of icosahedral SRO strongly depends on the alloy composition as displayed in Fig. 4. With

† typically from x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS)
increasing Cu-content, the fraction of FI-clusters (index $<0,0,12,0>$) as well as the fraction of distorted icosahedra (index $<0,2,8,2>$) increases significantly, while the fraction of other Cu-centered atomic clusters decreases. According to recent simulation studies, the MRO in Cu-Zr glasses can be characterized in terms of a string-like network of interpenetrating FI-clusters [30, 35, 46]. The connectivity of these network structures was found to depend on the alloy composition.

### 1.2 Plastic Deformation of Metallic Glasses

In general, plastic deformation in metallic glasses can be understood as a biased accumulation of local strains arising from atomic rearrangements. Depending on the temperature, the applied strain rate, and the properties of a specific MG, these local events can be distributed homogeneously or inhomogeneously in time and space [4], as shown in the deformation map in Fig. 5.

---

**Figure 5:** Deformation map as published in [4]. The absolute stress values are given for the specific glass $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$. (Reprint from Acta Materialia 55, 4067 (2007), © 2007, with permission from Elsevier.)
1.2 PLASTIC DEFORMATION OF METALLIC GLASSES

1.2.1 Atomic scale deformation mechanisms

In the last decades, a number of theories has been developed that account for the heterogeneous nature of plasticity in bulk metallic glasses. In the 1970s Spaepen [47] introduced a flow mechanism which is driven by individual atomic jumps in the presence of free volume sites as a result of an applied shear stress (Fig. 6(a)). Excess free volume is created by shear-induced structural disordering which leads to strain softening, a lower viscosity and consequently strong shear localization. This model, however, does not explain the atomic processes within shear bands during plastic flow and it is not consistent with more recent simulation results, demonstrating that the fundamental deformation mechanism in metallic glasses involves multiple atoms [48, 49]. A few years later Argon [50] presented the concept of shear transformations as the fundamental process of plastic flow, which is still widely used to model plastic deformation in metallic glasses [51, 52, 53]. A shear transformation (ST) is a thermally activated defect in a metallic glass, which initiates around free volume sites under an applied shear stress (Fig. 6(b)). This mechanism involves groups of atoms within a distance of about 5 atomic diameters and it closely resembles the nucleation of a dislocation loop in a crystal. In the potential energy landscape concept (see Fig. 2), an isolated shear transformation confined within the elastic matrix corresponds to a fast \( \beta \)-transition, while the percolation of several shear transformation, which leads to a collapse of the confining matrix and a breakdown of elasticity, is associated with a slower \( \alpha \)-transition [54]. Falk and Langner [48, 55] have developed a dynamic theory of shear transformation zones by extending Spaepen’s and Argon’s models. Their work reveals that plastic deformation in metallic glasses is achieved by multiple local shear events. This is in agreement with the cooperative shearing model proposed by Johnson and Samwer [56], which is inspired by Frenkel’s analysis of the shear strength of crystals. Their results suggest that the yield strength of a metallic glass is determined by the cooperative shear motion of STZs and that yielding occurs when a critical fraction of unstable STZs leads to global instability. Recent studies employing molecular dynamics simulations relate the mechanical properties of metallic glasses and their atomic structure: Cheng and co-workers

![Figure 6: Schematics of atomistic deformation mechanisms: (a) individual atomic jump as proposed by Spaepen [47] and (b) shear transformation according to Argon [50] (reproduced from reference [4]).](image)
metallic glasses [31, 43] have identified the full-icosahedral atomic clusters in amorphous Cu-Zr-alloys to strongly influence the dynamics and, consequently, strength and plasticity. Icosahedral packing of atoms corresponds to higher configurational transition barriers which leads to a higher resistance to shear transformations and hence reduced plasticity. The icosahedral units were found to form a string-like network penetrating the glass structure and, due to their high shear stability, the FI-network is assumed to serve as a structural backbone [35, 30, 46]. The surrounding matrix consists of fragmented clusters which behave liquid-like and, therefore, the FI-backbone is expected to determine the mechanical properties of the glass and the operating deformation mechanism, which was already predicted in an earlier study by Shi and Falk [57]. In this concept, alloys with a lower population of full icosahedra, where a bigger fraction of the material behaves liquid-like, are assumed to be more ductile.

1.2.2 Strain localization

Although there is a broad consensus that STZs are the basic units of plastic deformation in metallic glasses and that yielding involves a critical number of STZs, the question how the operation of single STZs in a material leads to the formation of an extended shear band (SB) is still under debate. One mechanism, which has been proposed, is shear band nucleation by the condensation of many STZs along a viable shear path [4]. This mechanism is supported by experimental results from Packard and Schuh [58], who observed that satisfying the yield criterion in just one point is not sufficient for shear band nucleation. Instead, the yield stress must be exceeded along a whole shear path. They assume, therefore, the formation of shear bands in metallic glasses to be a fundamentally cooperative process requiring many STZs to operate in concert. The other prominent candidate is shear band formation by intense shear accumulation in a small volume, which then propagates as a shear front across the shear plane, analogous to the nucleation and propagation of a dislocation [4]. This mechanism has been observed in recent studies employing atomistic simulation: Cao et al. [59] have simulated the tensile deformation of samples with free surfaces and observed shear band nucleation sites to develop mostly at the surfaces. The shear band nuclei were found to propagate from the surface through the sample in a “dislocation-like” shear front causing structural softening along a maximum stress path [59]. This is in good agreement with experimental results by Yang et al., who found a tendency for shear bands to nucleate from the specimen surface [60]. It is generally assumed that the homogeneous nucleation of shear bands would never occur in practice [61, 6] since shear bands would always form at a free surface before the theoretical yield stress is reached. Li and Li [62] even claim metallic glasses to be intrinsically ductile. Their results suggest that shear banding and brittle failure are caused
only by extrinsic factors, such as surface flaws or crystal phase formation, which introduce local stress concentrations and, consequently, localized deformation.

1.2.3 Homogeneous deformation

While at low temperatures plastic deformation usually occurs highly localized in narrow shear bands, metallic glasses have a large capacity for homogeneous plastic deformation and even superplasticity [63] at low strain rates or low applied stress, respectively, and elevated temperatures (see Fig. 5). Close to the glass transition and in the supercooled liquid, homogeneous flow is typically Newtonian, where the shear stress is directly proportional to the strain rate [64]. If the strain rate is increased and/or the temperature is decreased, a transition to Non-Newtonian flow occurs [65], which is attributed to a structural breakdown that cannot be recovered in the available relaxation time and leads to a decrease in viscosity.

Recently, Schuh and co-workers discovered a second regime of homogeneous flow for metallic glasses deformed at low temperatures and high strain rates [51]. In nanoindentation experiments they observed homogeneous deformation if the applied strain rates exceeded the characteristic rate for shear band nucleation, kinetically forcing homogeneous strain distribution. Based on their observations they proposed a new deformation map containing a temperature-dependent regime at high strain rates where homogeneous deformation occurs. The existence of a second homogeneous flow regime was supported by results from Yang and Nieh [66] who performed nanoindentation tests using a wide range of strain rates. Their data give evidence for a critical strain rate in the range of \(10^3 \text{s}^{-1}\) defining the transition to a second homogeneous flow region.

1.3 Influence of structural inhomogeneities

Despite a variety of interesting mechanical properties, metallic glasses have still not found their niche amongst conventional engineering materials. One of the reasons why up to today metallic glasses can hardly be found in structural applications is their strong tendency for strain localization and lack of ductility leading to macroscopically brittle failure at room temperature. In order to overcome this problem, different strategies are applied ranging from microstructure design to synthesizing composite materials and utilizing size effects. This section provides an overview of current progress in this field of research.

1.3.1 Composite materials: enhanced plasticity and toughness

One promising way to increase the plasticity of bulk metallic glasses is to develop heterogeneous microstructures by combining a glassy matrix with a crystalline second phase [5]: Experimental studies have revealed a significantly increased
plasticity at room temperature for BMGs containing homogeneously dispersed nanocrystals [67, 68]. This effect was attributed to the formation of multiple shear bands in the presence of nanoscale precipitates, which improves the resistance against catastrophic crack propagation. In order to get a better understanding of the underlying mechanisms, Shi and Falk applied molecular dynamics (MD) simulations [69] to study the uniaxial compression of a monoatomic amorphous model system containing nanocrystallites and observed the operation of multiple shear bands in the case of composite samples, which is in good agreement with experimental results. The amorphous-crystalline interfaces were found to promote the shear band nucleation; moreover, the crystalline particles acted as obstacles for shear bands hindering their propagation. Lund and Schuh [70] have studied the influence of the precipitate diameter using MD simulations and found that the strengthening effect is determined by the dislocation mechanisms operating in the nanocrystals. A persistent strengthening beyond the initial yield point is only obtained if the nanocrystals deform by homogeneous dislocation nucleation, which is the case if the crystallite size is at least twice the shear band thickness.

Another route to synthesize composite microstructures are so-called in-situ composites, which contain in-situ-formed crystalline dendrites in an amorphous matrix (Fig. 7). The ductile dendritic phase stabilizes the material against catastrophic failure and increases the ductility by developing a highly organized pattern of multiple shear bands distributed uniformly throughout the BMG [71, 72, 73, 74, 75].
Recently, an extraordinary tensile ductility has been reported for amorphous-crystalline nanolaminates consisting of amorphous Cu-Zr- and crystalline Cu-layers. The remarkable increase from zero tensile ductility for the monolithic bulk amorphous phase to \( \geq 4\% \) [76] or even \( \geq 13\% \) [77] for the nanolaminate samples was attributed to a size effect: if the thickness of the amorphous layers is smaller than the size of a shear band nucleus or the shear band width, respectively, than shear band formation is suppressed (the nucleus size as well as the shear band width are in the range of 10-20 nm [66, 78]). MD Simulations by Wang et al. [79] revealed that in laminates with 5 nm amorphous Cu-Zr- and 10 or 35 nm crystalline Cu-layers dislocations were nucleated from the amorphous-crystalline interfaces, which was often triggered by shear transformation zone activity in the adjacent glass layer. Additionally, they found that dislocations were absorbed in the glass-crystal interfaces, which lead to interface sliding and the activation of STZs.

1.3.2 Improved ductility by pre-plastic deformation

Another approach to enhance the plasticity of bulk metallic glasses is to pre-introduce a high density of shear bands by prior plastic deformation such as cold rolling [80, 81, 82], compression [83, 84], or severe plastic deformation [85]. The pre-deformation leads to a pseudo-composite structure consisting of a softer phase inside pre-induced shear bands and a harder phase in the undeformed regions. These micro-structural features improve the macroscopic plasticity by promoting the nucleation of secondary shear bands and shear band branching, as well as by limiting shear band propagation due to the intersection of shear bands.

1.3.3 Brittle to ductile transition at the nanoscale

Not only the presence of second phases and pre-induced shear bands can enhance the homogeneous plasticity of metallic glasses. Even monolithic amorphous alloys exhibit intrinsic ductility [86, 87, 88, 89, 90]: Recent experiments suggest a transition in deformation mode, from shear banding to a more homogeneous plastic deformation, if sample dimensions reach the nanometer regime. In uniaxial compression experiments, Volkert and co-workers found metallic glass–columns with a diameter below 500 nm to deform homogeneously [86]. Chen et al. observed a transition from highly inhomogeneous to fully homogeneous deformation in microbending tests if sample diameters were as low as 200 nm [87]. Extensive uniform elongation and necking were observed in in-situ tensile tests of small-volume metallic glass samples \( (d \approx 100\, \text{nm}) \) by Guo and colleagues [88]. Similar results have been reported by Jang and Greer, who found pillars with a diameter of 100 nm to deform homogeneously under uniaxial tensile load [89]. In a recent study by Luo and co-workers, metallic glass with dimensions smaller than 20 nm...
exhibited a remarkable tensile ductility of about 200% and, after necking, even the formation of an atomic chain was observed [90].

Despite the growing number of reports on size-dependent plasticity, doubts about the intrinsic nature of the size-effect remain. When it comes to mechanical testing of nanoscale specimen, experimental artifacts due to tapering of cylindrical pillars for compression tests, surface modifications during sample preparation by focused ion beam, and in-situ tensile specimen which are not free-standing, can change the operating deformation mechanism and, therefore, lead to false assumptions about the intrinsic materials properties. Moreover, size-independent deformation behavior and shear banding for sample-diameters as low as 150 nm has been observed for different metallic glasses [91, 92, 93], which is in clear contrast to the findings mentioned above. Recent simulation results support the picture of size-independent shear banding: Shi has simulated the tensile deformation of amorphous nanowires and found samples with a diameter of only 7.5 nm to form dominant shear bands during deformation [94]. His results suggest that shear band formation is size-independent until sample dimensions approach the shear band thickness. The discrepancy between their results and an earlier study by Li and Li, who observed solely homogeneous deformation for simulated nanowires and even claim metallic glasses to be intrinsically ductile [62], is attributed to the different sample preparation routine. Cylindrical samples which are cut from bulk samples at low temperature, like in the study by Li and Li, appeared to deform homogeneously before neck formation. Samples prepared by simulating casting, however, which are characterized by relaxed surfaces, deformed by shear banding.

1.4 OPEN QUESTIONS

Based on the existing knowledge on the structure and mechanical properties of metallic glasses as presented in this chapter, several open questions can be formulated. These questions will be addressed in the following and the order of the topics given below is a guideline for the structure of this thesis.

Simulation of metallic glasses with MD

- **What are suitable simulation conditions for simulating melt quenching?**
  Owing to the limited time scales accessible in MD simulations, the cooling rates used during glass preparation are several orders of magnitude higher than in experiments. It is important to determine simulation conditions which yield metallic glass structures that compare to laboratory made samples and can reproduce metallic glass properties. (Chapter 3)
• **How can we characterize the atomic level structure of metallic glasses?**
  Other than in the case of crystalline materials comprising a long range translational symmetry, the structural characterization of amorphous materials asks for alternative analysis techniques that are more sensitive to the local topology. The Voronoi tessellation method is a useful tool for analyzing the short range order of amorphous systems; however, for characterizing order beyond the first coordination shell or chemical ordering, additional characterization methods have to be used. (Chapter 4)

• **What are suitable conditions to simulate shear banding with MD?**
  For studying shear banding under tensile deformation with MD it is necessary to determine under which conditions (strain rates, temperatures, boundary conditions) shear banding is the dominant deformation mode in virtual samples. At the beginning of the studies presented in this thesis, there were no reports in literature on the simulation of shear bands in homogeneous samples under tensile deformation. At that point, shear banding had only been simulated in pure shear or in the presence of notches acting as stress concentrators. (Section 5.2)

**Shear banding in metallic glasses**

• **Is shear banding an intrinsic metallic glass property?**
  As mentioned above, in previous work shear banding was simulated in the presence of stress concentrators or free surfaces. A study on the homogeneous nucleation of shear bands and a comparison between homogeneous and heterogeneous nucleation is still missing. (Section 5.3)

  Moreover, recent experimental and simulation studies find nanoscale metallic glass specimens to deform homogeneously, which is attributed to the intrinsic ductility of metallic glasses. Other studies, however, claim that even metallic glass nano-samples deform by strain localization. These discrepancies ask for a systematic study on size-dependent plastic deformation of metallic glasses. (Chapter 6)

**Structural damage during plastic deformation**

• **How is the glass structure damaged during plastic deformation?**
  Although a number of studies exists on the structural damage caused by plastic deformation, most studies focus on structural defects in small systems which were deformed homogeneously. There is no comprehensive study analyzing the defects in CSRO, TSRO and MRO in a shear band and hardly any discussion on how general the findings are with respect to different alloy compositions. Moreover, it is still an open question which
metallic glasses

defect(s) are a pre-requisite for strain localization and which defects result from plastic straining. Another aspect, which is still up for discussion, is the existence of a percolated structural backbone in metallic glasses and its influence on plastic deformation. (Chapter 7)

• Why do SBs not recover instantaneously when subjected to thermal annealing?
In the framework of free volume theory, it is rather surprising that shear bands do not recover instantaneously when subjected to thermal annealing at high temperatures. Due to the increased free volume in shear bands, at high temperatures the local atomic mobilities and relaxation times should resemble the supercooled liquid, leading to fast recovery of structural defects. However, experimental observations contradict this (e.g., [95]). This inconsistency begs the need for a detailed investigation on thermal annealing of deformed metallic glasses to elucidate the atomic scale mechanisms involved in structural relaxation. (Chapter 8)

Improved ductility of BMGs with structural inhomogeneities

• Is there a method to systematically introduce structural inhomogeneities in a BMG-sample?
It was found that pre-deformation, like cold-rolling, leads to a pseudo-composite structure consisting of a softer phase inside pre-induced SBs and a harder phase in the undeformed regions. These microstructural features improve the macroscopic plasticity and it is an interesting questions whether there are other routes to produce metallic glasses with structural inhomogeneities and improved plasticity. One alternative method for synthesizing metallic glasses is powder consolidation, which supposedly yields BMGs consisting of glassy grains separated by interfaces [96]. Insights in the atomic level structure of glass-glass interfaces are still missing and the stability of the interfaces under compression and thermal annealing has not been studied before. (Chapter 9)

• How do glass-glass interfaces affect the mechanical properties of nanoglasses?
Although the idea of metallic nanoglasses with diluted interfaces was first introduced more than 20 years ago [96], there has not been a study investigating the mechanical properties of nanoglasses and the influence of glass-glass interfaces on the operating deformation mechanisms. (Chapter 10)

Before addressing the questions posed above, the following chapter provides an overview of the computational methods applied in the framework of this thesis.
METODS

2.1 MOLECULAR DYNAMICS SIMULATION

Atomistic simulations provide unique insight into atomic-scale processes in materials and are an important tool to explore structure-property relationships in metallic glasses [4]. Particularly for elucidating, e.g., the connection between local topology and potential STZs, the structural evolution inside shear bands, or intrinsic size effects in SB behavior, there is a need for molecular dynamics simulations.

2.1.1 Basic principles

Molecular dynamics (MD) simulations provide a method to study the dynamics of an ensemble of atoms. The atomic interactions are specified by interatomic potentials. For a given set of initial atom positions \( r_i \) and momenta \( p_i \), the properties of interest along the atomic trajectories can be determined by solving Newtons’ equation of motion

\[
F_i = \frac{\partial^2 r_i}{\partial t^2}, \quad i, j = 1...N,
\]

for each atom over a short timestep \( \delta t \); the interatomic forces are obtained as the gradient of the scalar potential \( V(\{r_j\}) \)

\[
F_i = -\nabla_i V(\{r_j\}),
\]

where \( m_i \) is the mass of atom \( i \) and \( F_i \) is the force acting on it. This leads to

\[
-\nabla_i V(\{r_j\}) = m_i \frac{\partial^2 r_i}{\partial t^2},
\]

The MD approach is a numerical solution of the classical many-body problem, since an analytical solution for more than three atoms does not exist [97]. It is assumed that the atomic forces are constant for one integration timestep. Thus the timestep is only in the range of a few femtoseconds and the accessible time
scales are typically a few nanoseconds \([98]\). A spatial discretization, however, is admissible to parallelize MD simulations in order to simulate larger ensembles. Hence simulations with system sizes up to billions of atoms can be realized \([99]\). While these system sizes are sufficient to simulate nanostructures like nanoparticles or nanowires, macroscopic samples contain on the order of \(10^{23}\) atoms, which cannot be realized with MD methods at present. This rises the question, how large a model system has to be to realistically reproduce the behavior of a macroscopic sample. In a system of macroscopic size, only a very small fraction of atoms is close to a surface and, therefore, exposed to a deviation from the environment prevailing in the sample interior. The smaller a system gets, the higher the fraction of ‘boundary-atoms’; in a system containing 500,000 atoms, approximately one quarter of the atoms is close to a boundary. Therefore, the simulation will fail to capture the typical state of an interior atom and the results will be strongly influenced by the system size. The goal for obtaining realistic simulation results must be the elimination of the effect of free surfaces. This can be achieved by applying periodic boundary conditions \([97]\). The use of periodic boundary conditions introduces identical images of the volume under observation (simulation box) arranged like an infinite space-filling array in three dimensions. One consequence of this periodicity is that an atom that leaves the system during the simulation reenters through the opposite side. Additionally, atoms within a certain distance of the boundary are able to interact with atoms in an adjacent copy of the simulation box and respectively with atoms near the opposite boundary.

The simulations presented in this study were performed with the open source molecular dynamics code LAMMPS (http://lammps.sandia.gov) \([100]\). By supporting massively-parallel simulations on large computing clusters, LAMMPS enables the simulation of multi-million atom systems over a physical time of nanoseconds, as required for the studies presented in this thesis.

2.1.2 Interatomic potentials

The interatomic potential, which is the most important input to any MD simulation, describes the dependence of the potential energy of a system on the atom coordinates. In a simple approach, these interactions occur between pairs of atoms and are responsible for the two principal features of an interatomic force. The first is a resistance to compression, hence the interaction repels at close range. The second contribution is an attractive one, which causes the binding of atoms in the solid state \([98]\). These characteristics are reproduced by potential functions that can adopt various forms and provide realistic models for materials to be used in MD simulations. Which interatomic potential is chosen for a certain simulation depends on the material and the properties that are to be reproduced. Historically, pair potentials, like the Lennard-Jones potential \([101]\), have been
utilized for the simulations of various problems, since they are computationally simple. Some significant problems, however, may arise when applying pair potentials to problems where the local environment is substantially different from the uniform bulk [102]. This includes problems involving, e.g., surfaces and grain boundaries, which applies for the present study. Common alternatives which are more suitable for simulating metallic materials are potentials in the format given by the embedded atom method (EAM) [103] and the Finnis-Sinclair (FS) scheme [104]. Although based on rather different physical approaches, both schemes yield similar models.

For the current study we have employed the interatomic potential for Cu–Zr as proposed by Mendelev et al. [105]. The potential is a semi-empirical many-body potential of the form proposed by Ackland and Vitek [106], which is based on a Finnis-Sinclair model. The FS model is based on a second-moment approximation to the tight-binding density of states for transition metals and it was extended by Ackland and Vitek, who incorporated the inter-species interaction. In this formalism, the total energy takes the following form:

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \phi_{t_it_j}(r_{ij}) + \sum_{i=1}^{N} \Phi_{t_i}(\rho_{i}), \quad (2.4)$$

where $t_{i/j}$ is the elemental type of atom $i/j$, $\phi_{t_it_j}(r_{ij})$ is the pair-wise potential, $\Phi_{t_i}(\rho_{i})$ is the embedding energy function and

$$\rho_{i} = \sum_{j} \psi_{t_it_j}(r_{ij}), \quad (2.5)$$

where $\psi_{t_it_j}(r_{ij})$ is the density function. Potentials of this type can properly describe the structural stability of alloys as a function of concentration and are capable of modeling alloying behavior like solid solutions, ordering, and demixing. The Cu–Zr potential was developed particularly for describing the atomic interaction in amorphous Cu–Zr alloys and it was found that the potential predicts the amorphous alloy structure in good agreement with x-ray diffraction data. Furthermore, a study on the elastic properties of different Cu–Zr glasses ($x_{Cu} = 0.33 – 0.65$) revealed that Young’s modulus, Poisson ratio, shear and bulk modulus of the amorphous alloys was in reasonable agreement with experimental data and the composition dependence of the elastic properties was predicted correctly [107]. Hence, they conclude that the potential is suitable for simulating other mechanical properties and the deformation behavior of Cu–Zr glasses.

2.1.3 Simulation of mechanical testing

For studying plastic deformation of metallic glasses, we simulate displacement controlled tensile tests, which is a typical setup used in experiments (e.g., [88, 89]).
Figure 8: Sample geometries for simulating tensile tests: (a) Nanowires are simulated with periodic boundaries along the tensile axis (z) and open boundaries are chosen laterally; (b) slab-shaped samples are deformed in z-direction, while the lateral boundaries are either both periodic (3dp), or periodic in y- and open in x-direction (2dp).

Other than in experiments, where tensile deformation is applied by displacing the ends of a sample relative to each other, in simulations the whole sample is deformed by homogeneously rescaling all atomic positions, which leads to the introduction of body forces. If a system is not homogeneous, e.g., in the presence of grain boundaries or second phases, it is not reasonable to rescale the relative distances uniformly due to possible differences in elastic moduli, and the dynamical response of the system may be altered [108]. For the case of homogeneous metallic glass samples we consider this effect to be negligible. Nanoglasses, which are studied in Part V, contain internal interfaces. However, the difference in elastic moduli between samples with and without interfaces is not significant (see Fig. 59) and, hence, we do not expect a strong influence of the way the sample is deformed on the deformation behavior.

As shown in Fig. 8, the samples are stretched along the z-direction using a constant engineering strain rate. In the case of nanowires (Fig. 8 (a)), lateral contraction in the x- and y-directions is facilitated by open boundaries. If x- and/or y-direction are periodic, like in a slab geometry (Fig. 8 (b)), the lateral sample dimensions are adjusted using a Berendsen barostat [109] such that the corresponding components of the stress tensor $\sigma_{xx}/\sigma_{yy}$ are zero. In order to achieve constant pressure, all atom coordinates in the sample are rescaled homogeneously by the barostat. The temperature during deformation is controlled using a Berendsen thermostat [109]. This simulation setup corresponds to a mixed ensemble, namely constant volume–constant temperature (nvt) in the
loading direction, and constant pressure–constant temperature (npt) in the lateral directions.

The deformation of nanowires, as illustrated in (Fig. 8 (a)), is presented in Chapter 6. Slab-shaped samples, like the one shown in (Fig. 8 (b)), either with fully periodic boundaries, or with open boundaries in x-direction, are investigated in Chapters 5, 7, 8, 9 and 10.

2.2 CHARACTERIZATION

One of the major challenges when studying metallic glasses is how to effectively characterize the amorphous structure and extract the key structural features which are relevant for glass formation and materials properties [110]. Unlike for crystalline materials, where the atomic structure can be identified in terms of lattice constants and crystal symmetries, we have to find alternative measures to describe and distinguish amorphous structures.

2.2.1 Radial distribution function

The radial distribution function (RDF), also called pair distribution function or pair correlation function, is widely used for characterizing the structure of glasses and liquids. It represents the probability to find an atom in a certain distance $r$ from another atom chosen as a reference [13]. If the atomic species are not differentiated or in a monoatomic system, the RDF takes the form

$$g(r) = \frac{1}{4\pi r^2 \rho N} \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(r - |\mathbf{r}_{ij}|) \quad \text{with} \ i \neq j,$$

where $\rho$ is the number density of atoms, $N$ is the total number of atoms in the system and $|\mathbf{r}_{ij}|$ is the distance between atom $i$ and atom $j$. In a multi-component system comprising more than one species, the so-called partial radial distribution functions (PRDF) can be calculated according to

$$g_{\alpha\beta}(r) = \frac{N}{4\pi r^2 \rho N_{\alpha} N_{\beta}} \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \delta(r - |\mathbf{r}_{ij}|),$$

where $N_{\alpha/\beta}$ is the number of atoms of type $\alpha/\beta$. Typical examples for PRDFs of amorphous systems are shown in Fig. 11.

Structural information can be derived from the RDF by analyzing, e.g., peak positions, peak widths, and relative intensities. For amorphous materials, the short and medium range order is reflected in the peaks at smaller distances. Conventionally, it is assumed that the SRO contributes to the first peak, whereas the MRO accounts for structural features beyond the first peak up to distances of $r = 1 - 2$ nm [110]. This approach, however, does not allow to establish a unique description of the atomic configuration in real 3D-coordinates, since the RDF yields only a statistical average projection of the structure on one dimension [111].
2.2.2 Voronoi Analysis

In this work, the short range order and packing density of Cu–Zr glasses were analyzed using the Voronoi tessellation method [112, 113], which is a common method for characterizing the local topology in computer-simulated amorphous structures (e.g., [31, 35, 114, 115, 116]). The Voronoi tessellation divides the simulation cell into Voronoi polyhedra (VP) around each atom as shown in Fig. 9. A VP is defined as the minimal polyhedron whose planar faces bisect at right angles the lines joining an atom to its neighboring atoms. The shape of a VP reflects the arrangement of all neighbors of a given atom, which can be characterized by the Voronoi index \([n_3, n_4, n_5, n_6]\), where \(n_i\) denotes the number of \(i\)-edged faces of the VP. The number of faces of a VP equals the geometric coordination number of the center-atom.

The VP diagram, which is the sum of all VPs constructed for all atoms in the sample (yellow network in Fig. 9 (a)), splits in a unique manner the total sample volume into zones each owned by one single atom. The resulting Voronoi volumes can be utilized to investigate the local packing density and its variation.

2.2.3 Chemical short range order

The chemical short range order (CSRO) can be characterized by the nearest neighbor correlation index \(C_{ij}\) \((i, j = \text{Cu, Zr})\) [35], which compares the distribution of Cu- and Zr-atoms in the metallic glass to a statistical distribution:

\[
C_{ij} = \frac{p_{ij}}{p_{ij}^p} - 1, \tag{2.8}
\]
where \( p_{ij} \) is the probability of an atom of type \( i \) and an atom of type \( j \) to be neighbors in the analyzed structure, and \( p_{ij}^0 \) is the value for an uncorrelated distribution. This probability is calculated as \( p_{ij} = m_{ij} / p_{\text{total}} \), where \( m_{ij} \) is the number of nearest neighbor (NN) pairs of type \( ij \) and \( p_{\text{total}} \) is the total number of nearest neighbor pairs. The uncorrelated value is obtained from

\[
p_{ij}^0 = \begin{cases} \frac{n_i(n_j-1)}{2n_i n_j} & \text{for } i \neq j \\ \frac{n_i}{N(N-1)} & \text{for } i = j \end{cases},
\]

where \( n_{i/j} \) is the number of atoms of type \( i/j \) in the system and \( N \) is the total number of atoms. A negative value for \( C_{ij} \) indicates a negative correlation, which means that atoms of type \( i \) have on average less \( j \)-neighbors than in the statistical case, and vice versa.

### 2.2.4 Local atomic strain

For visualization of shear transformations and shear bands in deformed metallic glasses, we utilized the local shear strain \( \eta_{\text{Mises}}^i \) for each atom \( i \), as introduced by Shimizu et al. \[117\]. The calculation of \( \eta_{\text{Mises}}^i \) requires two atomic configurations, the current structure, which is to be analyzed, and a reference structure. First a local transformation matrix \( J_i \) is determined, from which the Lagrangian strain matrix can be calculated as

\[
\eta_i = \frac{1}{2} (J_i J_i^T - I).
\]

The local shear invariant of atom \( i \) is then calculated as

\[
\eta_{\text{Mises}}^i = \sqrt{\eta_{yz}^2 + \eta_{xz}^2 + \eta_{xy}^2 + (\eta_{yy} - \eta_{zz})^2 + (\eta_{xx} - \eta_{zz})^2 + (\eta_{xx} - \eta_{yy})^2}. \tag{2.11}
\]

According to Shimizu et al., \( \eta_{\text{Mises}}^i \) is a good measure of local inelastic deformation, which is suitable to quantify the plastic deformation in metallic glasses on the atomic scale.

Based on this definition, Cheng et al. \[32\] proposed a parameter which reflects the degree of strain localization:

\[
\psi = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\eta_{\text{Mises}}^i - \eta_{\text{Mises}}^{\text{av}})^2}, \tag{2.12}
\]

where \( N \) is the number of atoms in the system, \( \eta_{\text{Mises}}^i \) is the atomic shear strain of atom \( i \), and \( \eta_{\text{Mises}}^{\text{av}} \) is the atomic shear strain averaged over all atoms in the system. A larger \( \psi \) value indicates larger fluctuations in the atomic strain and a more
localized deformation mode. The $\psi$-parameter allows a quantitative interpretation of strain localization and is applied in this work to compare the degree of strain localization in different samples.

In the present study, $\eta^{Mises}$ was calculated using the analysis and visualization software OVITO [118].
Part II

SIMULATION OF CU-ZR AMORPHOUS ALLOYS
As discussed in the introductory chapter (Sec. 1.1.4), the atomic structure of Cu–Zr glasses is not yet fully resolved. It is, therefore, not trivial to create appropriate structural models for computer simulations. In the case of crystalline materials, structural models can be built easily by the replication of a crystalline unit cell according to the specific translational symmetry. Since long range translational and orientational order are missing in metallic glasses, computer models have to be synthesized by other methods. The most common technique for simulating glassy systems is melt-quenching, where a melt of the desired composition is cooled below the glass transition temperature, similar to experiments. Due to the limited time scales accessible to MD simulations, however, the simulated cooling rates are several orders of magnitude higher than experimental cooling rates. It is, therefore, necessary to characterize the simulated glasses carefully and compare them to laboratory-made glasses if possible. Yet, this validation is difficult owing to the limited amount of structural information available from experiments.

Thus, the first part of this thesis is devoted to the preparation of adequate metallic glass samples and their characterization. After describing how we have simulated glass formation, the obtained glasses are characterized in terms of chemical and topological short range order as well as medium range order.
GLASS PREPARATION BY MELT QUENCHING

3.1 SIMULATION DETAILS

Most studies presented in this thesis were conducted using two different Cu-Zr-alloys in order to study the influence of composition on different materials properties: We studied a Cu-rich Cu$_{64}$Zr$_{36}$ alloy, which is known to have a high glass transition temperature, high packing density, high yield strength and low ductility [45]; the other alloy we considered is the Zr-rich Cu$_{36}$Zr$_{64}$ with a lower glass transition temperature and packing density, lower yield strength and higher ductility [119, 45].

For simulating glass formation by melt quenching, we first prepared simulation cells containing 8000 Cu-atoms on a simple cubic lattice and then randomly replaced Cu- by Zr-atoms to obtain the desired alloy composition. After melting, the samples were kept at a temperature of 2000 K for 2 ns to ensure chemical homogeneity and were subsequently quenched to 50 K using a constant cooling rate. The temperature was controlled using a Berendsen thermostat [109] and a Berendsen barostat [109] was applied to keep the pressure zero during quenching. In previous MD studies on metallic glasses, cooling rates between 0.01 and 10 K/ps have been simulated (see e.g.,[120]). As we would like to prepare glasses, which are as well relaxed as possible while still keeping the simulation times low, we decided to compare two cooling rates, namely 0.5 K/ps and 0.01 K/ps, the latter already being close to the limit accessible with MD at present.*

3.2 GLASS FORMATION

In Fig. 10 the change in average atomic volume (a,c) and average energy per atom (b,d) versus temperature is shown for the Cu-rich ($x_{Cu} = 0.64$) and the Zr-rich ($x_{Cu} = 0.36$) alloy during quenching with different cooling rates. The first thing which stands out is that a step is present in the volume-temperature as well as in the energy-temperature curves, evocative of a first order phase transition, if the

* Simulating the quenching of a sample containing 8000 atoms from 2000 K to 50 K with a rate of 0.01 K/ps takes four weeks on a machine with 4 onboard-CPU's.
melts are quenched with the lower cooling rate of 0.01 K/ps. Other than in the case of crystallization, however, where a sharp discontinuity occurs in volume and energy at the liquidus temperature, here the steps are rather smooth and span over an extended temperature interval of about 200 K. According to Angell [121, 122, 123] the shape of the glass transition strongly depends on the properties of the particular liquid and supercooled liquid (see also Section 4.2), and the glass transitions in, e.g., silicon or germanium show similarities to our slow-cooled MGs. For the higher cooling rate, the step is missing and the curves bend at the glass transition, similar to a second order phase transition, as it is expected for the formation of a metallic glass. In order to clarify whether a crystalline phase forms if the samples are quenched using the lower rate, we have calculated the partial radial distribution functions for all samples (Fig. 11). It is evident from the PRDFs that all samples are fully amorphous and no indications for the
Figure 11: Partial radial distribution functions for (a-c) Cu$_{36}$Zr$_{64}$-glasses and (d-e) Cu$_{64}$Zr$_{36}$-glasses obtained with different cooling rates.

The presence of a crystalline phase are found in any of the samples. Consequently, the steps observed in Fig. 10 do not correspond to the precipitation of a crystalline phase. We calculated the PRDFs of the Cu-rich alloy at different temperatures close to $T_g$, to take a closer look at the characteristics of glass formation during quenching with a low cooling rate of 0.01 K/ps (Fig. 12). Analyzing the curves
we find that the glass transition, which is indicated by a splitting of the second peaks [111], occurs around 1000 K. This is in good agreement with the glass transition temperature of 980 K given in literature for the same potential and alloy composition [119]. At temperatures below 900 K the features in the PRDFs hardly change, similar to the behavior of volume and temperature, where no further structural relaxation is observable below 900 K. Other than that, there are no
Table 1: Atomic density $\rho_0$, mass density $\rho$ and mean nearest neighbor distances $r_{ij}$ extracted from the PRDFs for simulated and laboratory-made glasses.

<table>
<thead>
<tr>
<th></th>
<th>$\rho_0$ [nm$^{-3}$]</th>
<th>$\rho$ [g · cm$^{-3}$]</th>
<th>$r_{\text{CuCu}}$ [Å]</th>
<th>$r_{\text{ZrZr}}$ [Å]</th>
<th>$r_{\text{CuZr}}$ [Å]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{36}$Zr$</em>{64}$</td>
<td>51.1</td>
<td>6.88</td>
<td>2.61</td>
<td>3.19</td>
<td>2.90</td>
<td>this work</td>
</tr>
<tr>
<td>(exp. Cu$<em>{35}$Zr$</em>{65}$)</td>
<td>51.2</td>
<td>7.01</td>
<td>2.63</td>
<td>3.16</td>
<td>2.80</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>6.69</td>
<td>2.53</td>
<td>3.18</td>
<td>2.77</td>
<td>[124]</td>
</tr>
<tr>
<td>Cu$<em>{64}$Zr$</em>{36}$</td>
<td>61.9</td>
<td>7.57</td>
<td>2.61</td>
<td>3.16</td>
<td>2.87</td>
<td>this work</td>
</tr>
<tr>
<td>(exp. Cu$<em>{65}$Zr$</em>{35}$)</td>
<td>63.7</td>
<td>7.75</td>
<td>2.63</td>
<td>3.08</td>
<td>2.75</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>7.55</td>
<td>2.55</td>
<td>3.04</td>
<td>2.72</td>
<td>[124]</td>
</tr>
</tbody>
</table>

indications in the PRDFs for any peculiarities during the glass transition which could explain the observed characteristics of a first order phase transition.

The glass transition temperature for the Zr-rich glass is determined by analyzing the splitting of the second peaks in the PRDFs (not shown), as well. We observe the splitting to occur between 800 K and 900 K, which is again in good agreement with the value of 840 K reported in literature for the same potential and alloy composition [119].

Interestingly, the PRDFs in Fig. 11 of the glasses prepared with different cooling rates look absolutely identical, despite the different features in the volume and energy curves. But, as already mentioned in Section 2.2.1, the RDF yields only a statistical projection of the structure onto one dimension and thus does not establish a unique description of the atomic configuration in real 3D coordinates [111]. The structural differences between the glasses prepared with different cooling rate will be revisited in the following chapter, where the chemical and topological order of the samples are characterized.

On the basis of the information provided by the volume-temperature curves as well as the PRDFs we can compare our glass samples to laboratory-made samples to get a first estimate how well the simulated structures reproduce reality and how the cooling rate influences the final structure. Firstly, we determined the atomic density $\rho_0$ and the mass density $\rho$ for both alloys and cooling rates. In agreement with the congruent PRDFs for samples produced with different cooling rates, the final volume of the samples is almost identical (see Fig. 10 (a) and (c)) and hence the density of our glasses are hardly influenced by the cooling rate. The resulting densities are $\rho_0 = 61.9$ nm$^{-3}$ and $\rho = 7.57$ g · cm$^{-3}$ for the Cu-rich glass, and $\rho_0 = 51.1$ nm$^{-3}$ and $\rho = 6.88$ g · cm$^{-3}$, for the Zr-rich glass. These values agree very well with experimental data given in Table 1. The position of the first peak in the PRDFs is a measure for the mean nearest neighbor distance $r_{ij}$, with
$i, j = \text{Cu, Zr.}$ We extracted the $r_{ij}$-values from the PRDFs in Fig. 11 and listed the results in Table 1. Again we find a good agreement with experimental data.

Comparing the PRDFs for the Cu-rich and the Zr-rich glass, we find that the nearest neighbor distances are independent of alloy composition within the error limits, while the interatomic distances of the second and higher neighbors are shifted to smaller distances for higher Cu-content. Mattern et al. [33], who observed a similar effect, attributed this shift to the densification of atomic packing with increasing Cu-content due to enhanced topological atomic ordering. Another feature that stands out when comparing the PRDFs of different pairs is that for both glassy alloys the first peak of unlike (Cu–Zr) pairs is relatively sharp as compared with those of like atoms (Cu–Cu, Zr–Zr). According to Chen and Waseda [124], this qualitatively suggests a preferred interaction of unlike atom pairs in amorphous Cu$_{36}$Zr$_{64}$ and Cu$_{64}$Zr$_{36}$.

### 3.3 Summary

To summarize this chapter, we simulated the melt-quenching of a Cu-rich Cu$_{64}$Zr$_{36}$ glass and a Zr-rich Cu$_{36}$Zr$_{64}$ glass. In order to estimate the influence of cooling rate on the atomic-level structure we have synthesized samples with two different cooling rates, 0.01 K/ps and 0.5 K/ps. When quenched with the lower rate, we detected a step in the volume- and energy-temperature curves at the glass transition for both alloys, similar to a smoothed first order phase transition; using the faster cooling rate, this feature did not appear. According to the PRDFs, all prepared samples were fully amorphous and the distribution functions were identical for both cooling rates. The density of the glasses was found to agree well with experimental data and for the cooling rates used in this study, no influence of the cooling rate on the material’s density was detected. A similarly good agreement with experimental data was found for the mean nearest neighbor distances extracted from the PRDFs. We observed a shift in the interatomic distances of the second and higher neighbors to smaller distances for higher Cu-content, which hints towards an enhanced topological ordering in the Cu-rich glass. Moreover, the sharp first peak in the PRDF for Cu–Zr pairs hints towards a preferred interaction of unlike atom pairs in both glassy alloys.

Despite the step in the cooling curves for the lower cooling rate, we did not detect significant differences between glasses quenched with 0.01 K/ps and 0.5 K/ps: the PRDFs were identical, and the final energies and densities were hardly influenced by the cooling rate. The following chapter provides a detailed analysis of local order in the different glassy samples and the influence of the cooling rate is revisited.
4.1 Chemical Short Range Order

In Fig. 13, the evolution of chemical short range order during melt-quenching is displayed in terms of the nearest neighbor correlation indices $C_{\text{CuCu}}$, $C_{\text{ZrZr}}$, and $C_{\text{CuZr}}$. A positive correlation index $C_{ij}$ indicates that the number of $j$-atoms surrounding an $i$-atom is, on average, larger than in the statistical case, and vice versa. According to Fig. 13, changes in the CSRO occur solely in the liquid and supercooled liquid regime and for temperatures below $T_g$ the chemical ordering remains unchanged. We attribute this to the significantly decreased atomic mobilities in the glassy state, since the establishment of chemical order requires

![Figure 13: Evolution of chemical short range order during melt quenching measured by the nearest neighbor correlation indices. (a-c) Comparison of different cooling rates for Cu$_{64}$Zr$_{36}$, and (d-e) CSRO-formation in different alloys prepared with a cooling rate of 0.01 K/ps.](image-url)
Figure 14: Distribution of coordination numbers of Cu- and Z-atoms for (a,b) a Cu$_{36}$Zr$_{64}$ glass and (c,d) a Cu$_{64}$Zr$_{36}$ glass, which were prepared with different cooling rates.

long range diffusion [95]. It is, therefore, not surprising that the degree of CSRO, which is reached for the higher cooling rate, is less pronounced, as observable in Fig. 13 (a-c). During quenching, the fraction of Cu-Cu bonds decreases in both alloys (Fig. 13 (d) and in the final glasses, $C_{CuCu}$ is negative, which is more pronounced for the Zr-rich glass. At the same time, the fraction of Zr-Zr bonds in the final glasses is higher than expected from the global composition (Fig. 13 (e) and, particularly for the Cu-rich glass, we find also the unlike Cu-Zr bonds to be favored (Fig. 13 (f). These results support the assumption of a preferred interaction of unlike atom pairs from the partial radial distribution functions in Section 3.2.

For characterizing the topological short range order (TSRO) we have employed the Voronoi analysis, which yields a Voronoi volume for each atom, the coordination number and a Voronoi index reflecting the topology in the first coordination shell of an atom.
4.2 TOPOLOGICAL SHORT RANGE ORDER

Our results on the chemical order in Cu$_{36}$Zr$_{64}$ an Cu$_{64}$Zr$_{36}$ glass are in good agreement with experimental findings by Ma et al. [125], who investigated different Cu–Zr glasses and found that around Cu, the unlike Cu-Zr bonds are favored, while around Zr, the fraction of Zr-Zr bonds is higher than expected from the global composition.

In Fig. 14, the distribution of coordination numbers is displayed for both alloys and cooling rates. Firstly, the influence of cooling rate on the coordination numbers is negligible for the cooling rates used in this study. For both alloys we find that 12 is the most frequent coordination number of Cu-atoms. The average coordination number of Cu-atoms is $N_{Cu} = 12.5$ in the Cu-rich alloy and $N_{Cu} = 11.6$ in the Zr-rich alloy, which is in excellent agreement with experimental values reported by Mattern et al. [33], who found values of $N_{Cu} = 12.5$ for Cu$_{65}$Zr$_{35}$-glass and $N_{Cu} = 11.5$ for Cu$_{35}$Zr$_{65}$-glass. For the Zr-atoms our analysis yields 16 as the most frequent coordination number in the Cu-rich glass and 15 in the Zr-rich glass. This trend for higher coordination with higher Cu-content, which is found also in the coordination numbers of Cu-atoms, is further reflected in the average coordination numbers, where we find $N_{Zr} = 16.0$ for the Cu-rich glass and $N_{Zr} = 15.2$ for the Zr-rich glass. The experimental values in Ref. [33] are slightly lower with $N_{Zr} = 14.6$ for Cu$_{65}$Zr$_{35}$ and $N_{Zr} = 13.1$ for Cu$_{35}$Zr$_{65}$, the trend for increasing coordination numbers with higher Cu-content, however, is the same. This fits very well to the densification of atomic packing with increasing Cu-content which we assumed from the comparison of the radial distribution functions in Section 3.2.

In order to learn more about the topology, we have analyzed the frequency distribution of Voronoi polyhedra occurring in our Cu–Zr glasses. Fig. 15 shows

![Figure 15](image-url)
the population of the dominant types of Cu- and Zr-centered atomic clusters, which occur with a frequency of at least 3% in one of the glasses. The frequency distribution is in good agreement with other simulation studies reported in literature (e.g., [43, 116]). When summing up the fractions of atoms located in a cluster of dominant type (= the ones displayed in Fig. 15), it stands out that in both alloys about 70% of the Cu-atoms are located in a cluster of dominant type, while only 40% of the Zr-atoms are located in a dominant cluster. According to Chen and Ma [110], this indicates that Cu-centered clusters are the efficiently packed characteristic structural unit in Cu–Zr glasses with well defined topological SRO.

A common feature of the Voronoi indices* in Fig. 15 is the dominance of five-edged faces, for Cu- and Zr-centered clusters in both alloys. This was observed in other simulation studies before and it was found that five-fold symmetry is indicative of dense atomic packing [45, 116].

In the Cu-rich glass, the dominant cluster with a population of 22% is the Cu-centered full icosahedron with index [0,0,12,0]. As the cluster with the next smaller population, the icosahedron-like clusters with index [0,2,8,2] account for

* For the definition of the Voronoi index, see section 2.2.2.
14\% of the Cu-atoms. In the Zr-rich glass, on the other hand, the fraction of Cu-centered FLs is significantly reduced with only about 5\% and the majority of the Cu-atoms is located in clusters with index [0,2,8,0], [0,2,8,1], and [0,2,8,2]. According to Lee et al. [46], these icosahedron-like clusters act as glue-polyhedra providing better connectivity in forming FI-networks. Other than the Cu-centered FLs, however, which were found to determine properties like the glass forming ability and the strength of Cu-Zr amorphous alloys, icosahedron-like clusters appeared not to be decisive for these properties [31].

As already mentioned above, we find a broader distribution of the Zr-centered clusters in both glasses, and most clusters displayed in Fig. 15(b) are occupied by less than 10\% of the Zr-atoms. Compared to the Cu-centered clusters, the composition dependence of the population of most dominant Zr-centered clusters is less pronounced.

In order to elucidate the processes responsible for the differences in the cooling curves for different cooling rates in Fig. 10, we analyzed the evolution of TSRO during melt quenching. Fig. 16 shows the frequency distribution of the dominant Cu- and Zr-centered VPs at different temperatures during quenching with (a) 0.01 K/ps and (b) 0.5 K/ps. While the order in the relaxed melts at 2000 K (orange) is identical, we already observe a difference in the population of certain VPs at 1200 K (purple), which is still in the liquid regime. The fraction of Cu-atoms in FLs with index [0,0,12,0] is 7\% for the lower cooling rate compared to only 6\% for the higher cooling rate. The difference is even more pronounced for VPs with index [0,2,8,2], where we find 10\% for the lower cooling rate and 8\% for the higher cooling rate, or for VPs with index [0,3,6,4], where we find 9\% and 7\%, respectively. This is in agreement with Frank’s hypothesis [41] that metallic melts have a tendency for ordering which enables them to be undercooled. When using a high cooling rate, the melt does not have enough time to achieve the degree of ordering that corresponds to the particular temperature. Apparently, a cooling rate of 0.5 K/ps is so high, the decrease in temperature is faster than the kinetics for ordering. If a lower cooling rate of 0.01 K/ps is used, however, the high driving force for ordering in the supercooled liquid leads to the sudden creation of SRO, which is reflected in the strong increase in the fraction of FLs between 1200 K and 1000 K. The sudden ordering in this temperature interval can explain the step in the energy curves in Fig. 10.

4.3 MEDIUM RANGE ORDER

After characterizing the short range order, we will now go one step further and investigate how the SRO-units are arranged in the glass structure. In a recent publication, Li et al. [35] discovered that FL-clusters tend to aggregate by forming chains and network structures, and Lee and co-workers [46] identified that these network structures are formed preferentially by interpenetrating icosahedra. We
have, therefore, examined how the FI-clusters in our glasses are interconnected and how the connectivity of the network structures is influenced by alloy composition and cooling rate. Fig. 17 illustrates the properties of the MRO-network that were analyzed in this context: in Fig. 17 (a) and (b) two typical MRO-clusters of different size $n_{MRO} = 2$ and $n_{MRO} = 3$ are shown, each consisting of 2 or 3 interpenetrating FI-units, respectively. But by evaluating only the number of FI-units belonging to one MRO-cluster, the degree of cross-linking cannot be captured. This can be done, however, by determining the number of neighboring icosahedra $N_{FI}$ for each FI-center, i.e., how many neighbors in the first coordination shell are also centers of other icosahedra. This is illustrated in Fig. 17 (c), where only the FI-centers of an extended MRO-cluster are displayed and colored according to the number of FI-neighbors $N_{FI}$. A value of $N_{FI} = 0$ marks a single FI, $N_{FI} = 1$ marks a FI-unit at the end of a chain, $N_{FI} = 2$ means the FI-unit is located inside a chain and FIs with $N_{FI} > 2$ are highly cross-linked. By evaluating the frequency distributions and average values of the cluster size $n_{MRO}$ and the number of FI-neighbors $N_{FI}$, we can fully characterize the MRO-network present in our Cu–Zr glasses.

In Fig. 18, the FI-network structures are shown for a Cu$_{36}$Zr$_{64}$ and a Cu$_{64}$Zr$_{36}$ glass sample. A first visual analysis already reveals that in the Zr-rich glass (Fig. 18 (a)), a large fraction of the FI-units has no connection to other FIs, but clusters of several FIs are also observable. In the Cu-rich glass (Fig. 18 (b)) on the other hand, the FI-units are highly aggregated and the first impression is that the network could even be percolated.

For getting a quantitative impression of the dimensions of the FI-network structures, we have plotted the distribution of MRO-cluster-size $n_{MRO}$ for the

---

**Figure 17**: Images of MRO-clusters consisting of interpenetrating FI-units. In (a) and (b) FI-centers are displayed in red and atoms on the surrounding shell are displayed in blue. In (c) an extended MRO-cluster is displayed by showing only the FI-centers, which are colored according to their number of FI-neighbors.
Figure 18: Snapshots of FI-network in (a) Cu\textsubscript{36}Zr\textsubscript{64} and (b) Cu\textsubscript{64}Zr\textsubscript{36} glass. In the first and third row atoms which do not belong to a FI-cluster are deleted, FI-centers are displayed in red and atoms on the surrounding shell are displayed in blue. In the second and fourth row only the FI-centers are displayed and colored according to the number of FI-centers in the nearest neighbor shell \( N_{FI} \) (blue: \( N_{FI} = 0 \), red: \( N_{FI} = 6 \)).
Cu-rich and Zr-rich glasses prepared using a cooling rate of 0.01 K/ps in Fig. 19 (a). From the size distribution we learn that in the Cu_{36}Zr_{64} glass the majority of FIs is not connected to other FIs, and that clusters containing more than 10 FI-units do not occur. For the case of the Cu_{64}Zr_{36} glass, the distribution is much broader and most FIs are part of a MRO-cluster. Extended network structures comprising more than 10 FIs are common and the biggest cluster is formed by 52 individual FIs. In contradiction to the assumption of a percolated network of interpenetrating FIs, the size distribution reveals that despite a high degree of agglomeration individual MRO-clusters are the dominant structural feature in the Cu-rich glass. A fully percolated network would correspond to one very large cluster to span the whole simulation cell. To estimate the effect of cooling rate on the MRO we have calculated the average cluster size for all alloys and cooling rates: The average size of MRO-clusters in the Zr-rich glass prepared with a cooling rate of 0.01 K/ps is $n_{MRO}^{av} = 1.4$ compared to $n_{MRO}^{av} = 1.3$ for the same alloy prepared with a higher cooling rate. In the Cu-rich glass we calculated values of $n_{MRO}^{av} = 7.1$ for the lower cooling rate and $n_{MRO}^{av} = 5.6$ for the higher cooling rate. Although the effect is more pronounced for the Cu-rich alloy, we find a tendency towards smaller MRO-clusters if a glass was synthesized with a higher cooling rate.

Fig. 19 (b) shows the population of FIs with a certain number of FI-neighbors $N_{FI}$ on the first coordination shell. As already expected from Fig. 18, most FI-units in the Zr-rich alloy are isolated FIs with $N_{FI} = 0$, while the FI-units in the Cu-rich alloy are highly interconnected with a maximum at $N_{FI} = 2$ indicating
Figure 20: Influence of FI-connectivity on (a) average Voronoi volume of FI-centers and (b) average potential energy. The data shown are averages for FIs with the common compositions Cu$_7$Zr$_6$ and Cu$_8$Zr$_5$. (Dashed lines are meant as a guide to the eye and do not represent linear fits.)

a substantial number of chain-like clusters. Due to the high fraction of FIs in the Cu$_{64}$Zr$_{36}$ glass, however, a certain degree of connectivity is unavoidable and, therefore, we compare the distributions in Fig. 19 (b) with the distribution for random site occupation to determine whether the degree of cross-linking is higher than expected. For random site occupation, the probability of a FI-center to have $N_{FI}$ neighboring FIs among its 12 nearest neighbors is given by:

$$w(N_{FI}) = \binom{12}{N_{FI}} \cdot (f_{FI})^{N_{FI}} \cdot (1 - f_{FI})^{12-N_{FI}}, \quad (4.1)$$

where $f_{FI}$ is the fraction of atoms located in the center of a FI-unit relative to the total number of atoms in the system. The resulting distributions for both alloys are represented by the dashed yellow lines in Fig. 19 (b). Obviously, the degree of cross-linking between FI-units is higher than for a random distribution of FIs in both glasses, which is reflected in the shift of the distributions to higher $N_{FI}$-values. The networking of FIs appears to be favorable, which can be understood when analyzing the average Voronoi volume and potential energy of FI-centers as a function of $N_{FI}$ (Fig. 20). The resulting data reveal that the average Voronoi volume decreases with increasing number of FI-neighbors as well as the average potential energy. Consequently, a higher degree of cross-linking yields a higher local packing density and lower potential energy.

If a glass is prepared using a higher cooling rate, the degree of cross-linking is decreased as can be seen in Fig. 19 (b), where the green data-points were calculated for Cu$_{64}$Zr$_{36}$ quenched with 0.5 K/ps. This trend is also reflected in the average number of neighboring FIs, which is $N_{FI}^{0.01} = 2.56$ for the Cu-rich glass quenched with 0.01 K/ps and $N_{FI}^{0.5} = 2.42$ if the glass was quenched with 0.5 K/ps.
In the case of the Zr-rich glass we find values of $N_{FI}^{av} = 0.72$ for the lower cooling rate compared to $N_{FI}^{av} = 0.55$ for the higher cooling rate.

Taking into account these results, the main structural difference between the glasses prepared with different cooling rates is the connectivity of the MRO-network structures which lead to variations in the local atomic packing density and local potential energy. Interestingly, these differences on the atomic scale are not reflected in the macroscopic density or average potential energy or PRDFs of the corresponding glasses (see Chapter 3).

### 4.4 Summary

The structural characterization of glass samples with different alloy composition and cooling history provides detailed insights which form the basis for the following chapters, where the relationship between the structure and mechanical properties of Cu–Zr glasses are investigated. We found that the chemical short range order in both glassy alloys deviates from a statistical alloy and while for both glasses the fraction of Cu-Cu bonds is lower than expected from the global composition, Zr-Zr and Cu-Zr bonds appear to be favored. A higher cooling rate leads to a lower degree of ordering. In agreement with previous studies, the Cu-centered full icosahedron is a key structural motif in the topological short range order of Cu–Zr glasses. The fraction of FI-units in the Cu-rich glass is significantly higher than in the Zr-rich glass and the cooling rate influences the evolution of the icosahedral short range order. Interpenetrating FI-units were found to form extended network structures, which leads to locally increased packing densities and decreased potential energies. The cross-linking of FI-units is more pronounced in the Cu-rich glass and we found that a higher cooling rate produces glasses with, on average, smaller MRO-clusters and a lower degree of cross-linking.

According to our analysis, the differences between glasses prepared with different cooling rates are hardly detectable when comparing global quantities like the density or the average potential energy. On the atomic scale, however, glasses prepared with a cooling rate of 0.01 K/ps showed a higher degree of ordering, while still being fully amorphous. The densities and PRDFs of our glasses were found to be in good agreement with experimental data, as well as the CSRO. We were, however, not able to further validate the atomic structure of our samples, due to a lack of experimental data.

In the following chapters, only the glass samples quenched with a cooling rate of 0.01 K/ps will be investigated, which we assume to be more relaxed.