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Abstract

Materials scientists lack a general, abstract description of the atomic structure of metallic glasses (MGs). Structural descriptions developed for crystals and crystal defects are ineffective because the amorphous structure of MGs does not exhibit the necessary translation and rotational symmetries, and structure descriptions developed for oxide glasses are ineffective due to the lack of strong covalent bonds in MGs and the higher coordination number of local structures, which allows for more structural diversity.

This thesis reports research on improved abstract descriptions of MG structure developed by studying both the short- and medium-range order (SRO and MRO) of simulated MGs. Hybrid reverse Monte Carlo (HRMC) simulations were used to generate MG structures with realistic MRO and molecular dynamics (MD) simulations were used to generate MG structures with low energy. In Zr-Cu-Al, a metal-metal system, subcritical fcc-like MRO exists at the nanometer scale, and better glass forming alloys can be creating by destabilizing crystal-like SRO and MRO. In the Pd\textsubscript{82}Si\textsubscript{18} metal-metalloid system, an fcc-like region also exists, but the structure is more complicated and cannot be explained by typical topological structure metrics. A new structure metric called *motif extraction* based on geometry rather than topology was developed to characterize the local structure of MGs. Motif extraction applied to a canonical metal-metal glass, Zr\textsubscript{50}Cu\textsubscript{45}Al\textsubscript{15}, quenched via MD, reproduces results obtained from topological approaches and identifies a hierarchy of structures as a function of coordination number that is focused around icosahedral geometries, which are dominant in metal-metal glasses. An analogous hierarchy of structures is found in HRMC models of Zr\textsubscript{50}Cu\textsubscript{35}Al\textsubscript{15} that focuses around fcc geometries. This suggests that one or two motifs may fundamentally dominate the structure of both glassy and crystal-like SRO in MGs.
Applying motif extraction to a Pd$_{82}$Si$_{18}$ quenched via MD reveals a new local structure that correlates strongly with the glass transition. This motif has the same topology as another motif with opposing properties. A hierarchy of order is identified in HRMC models of Pd$_{82}$Si$_{18}$, analogous to the fcc-like hierarchy found in Zr$_{50}$Cu$_{35}$Al$_{15}$. Analysis of two Al$_{92}$Sm$_{8}$ MGs created using different synthesis techniques reveals MRO analogous to metal-metal and metal-metalloid glasses, including the fcc-like hierarchy of order, illustrating that fcc-like close-packed order may be ubiquitous in MG systems. The structures of the two Al$_{92}$Sm$_{8}$ glasses are distinguished by a higher fraction of fcc order in the glass synthesized using mechanical rolling, compared to the glass to synthesized via melt-spinning.

The final chapter reports experimental work identifying a new type of MRO structure in a-Si thin films. The new MRO is consistent with larger 8-atom rings rather than the 6-atom rings that are typically found in the structure of a-Si.
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1 Introduction to Glasses

1.1 Metallic Glasses: A Brief Introduction

Metallic glasses (MGs) are amorphous metal alloys with properties that combine the metallic bonding characteristics of metals with the amorphous structure of glasses. They are often multicomponent alloys, although recent studies synthesized monatomic MGs using extremely high cooling rates [1] or at high pressure [2]. The combination of metallic bonding and amorphous structure leads to a set of unique properties that are uncommon in other materials. For example, MGs can be strong yet elastic [3–5], corrosion resistant [6–8], and processed using thermoplastic forming [9,10], and some are biocompatible [11,12]. Controlling and predicting these properties, however, remains a difficult task due to a lack of understanding of the structure that controls properties in MGs.

Unlike molecular and oxide glasses with strong covalency, the atoms in MGs are connected via non-directional bonds and do not form molecules. Instead, the kinetics of MGs derive from the movement of individual atoms as they swap neighbors and diffuse through the material, resulting in a simpler kinetic picture of the material. Complexity arises from the large coordination numbers of atoms in MGs, ranging from ~ 8-16 [13], and their local structure is therefore more complicated than strongly covalent glasses which have coordination numbers typically ranging from 3-8 [14].

1.2 What is a Glass?

Glasses have become ubiquitous in our world, with applications ranging from consumer electronics [15], semiconductors [16], and optics [17–19] to everyday window glass, clean energy [20–22], and medicine [23–25]. These successes are largely due to our knowledge of oxide glass structure, and scientists can now design oxide glasses with specific properties due to a thorough understanding of their structure-property-processing relationships.
A glass is formed by cooling a material from its liquid state to a solid without inducing a first-order phase transition to a crystalline structure. Sufficiently high cooling rates are often required to avoid nucleation and growth, forcing the material into an equilibrium supercooled liquid state. As the temperature is decreased further, molecular motion slows down exponentially or super-exponentially until significant molecular motion stops at laboratory timescales (often considered to be ~100 s). The temperature at which this occurs is defined as the glass transition temperature, $T_g$, below which the material is in a solid, glassy state. Despite the transition from liquid to solid, all properties of the material change continuously and thus the transformation is not a thermodynamic first order phase transition. A typical curve for a liquid cooled at three different rates is shown in Figure 1.1. If the liquid is quenched slowly, crystals may nucleate and grow. If crystallization is avoided, the supercooled liquid falls out of equilibrium into the glassy state, which happens at lower temperatures for slower cooling rates. This is because the slower the supercooled liquid is cooled, the more time it has to find configurational states that are lower in enthalpy and therefore remain in equilibrium. The ability of a material to avoid crystallization and form a glass is termed its glass-forming ability (GFA), often measured for metals by the critical casting diameter of a rod-shaped sample as a proxy for the more difficult to measure critical cooling rate, $R_c$. $R_c$ is the threshold cooling rate at which a supercooled liquid forms a glass, and at which slower cooling rates will result in a crystal. Since homogeneous nucleation occurs stochastically, many measurements of the cooling rate are required to accurately measure $R_c$. 
As the supercooled liquid approaches \( T_g \), a number of important phenomena occur: 1) the viscosity of the material increases dramatically, in some cases by as much as 14 orders of magnitude [27–29]; 2) structural relaxations decouple into two different timescales [26]; 3) the entropy of the supercooled liquid decreases faster than the corresponding equilibrium crystal, leading to the Kauzmann entropy crisis [30] if dynamical arrest at \( T_g \) was avoided; and 4) dynamical heterogeneities become more prevalent [31–36].

In conjunction with the increase in viscosity, the \( \alpha \)-relaxation time \( \tau_\alpha \) increases and it has been widely shown that the viscosity, \( \eta \), is linearly proportional to \( \tau_\alpha \) according to \( \eta = G_\infty \tau_\alpha \) where \( G_\infty \) is the infinite frequency shear modulus. In fact, even for indomethacin, a very fragile glass (see Chapter 1.4 for a definition of fragility), \( \tau_\alpha \propto \eta^{0.99} \) [37]. This increase in viscosity and relaxation time is predicted to be inversely proportional to the diffusivity, \( D \), of the material via the Stokes-Einstein equation,

\[
D = \frac{k_B T}{6\pi \eta r}.
\]

However, as the temperature \( T \) approaches \( T_g \), this relationship breaks down in fragile glass formers [37,38], and \( D \) correlates more strongly with crystal grow rates [37] than viscosity.
The decoupling of structural relaxation as $T$ approaches $T_g$ is a ubiquitous feature of supercooled liquids. The slow relaxation mechanism (termed the $\alpha$-relaxation) dies out completely at $T_g$, while the fast $\beta$-relaxation remains present in the glassy state (Figure 1.2). The structural origins of these two relaxation mechanisms remain unclear; however, it is hypothesized that the $\alpha$-relaxation results from atoms or molecules moving approximately one interatomic or intermolecular diameter in distance [32], while the $\beta$-relaxation is believed to be the result of bond swapping [39].

![Image of decoupling of $\alpha$- and $\beta$-relaxations approaching $T_g$. Figure drawn from Ref. [26].](image)

The Kauzmann paradox [30] is one of the longest standing mysteries in glass science. It occurs when the entropy vs. temperature supercooled liquid curve is extrapolated past the glass transition to zero entropy, which occurs at a finite temperature $T_k$ for many glasses (Figure 1.3). Some consider the glass that would be formed at zero entropy to be an “ideal glass”, analogous to the minimum energy crystalline state. However, this implies that no motion of the atoms or molecules occurs despite a non-zero temperature, resulting in an apparent violation of the laws of thermodynamics. Recently, this paradox has been resolved by a statistical mechanics treatment
of the glassy state in which it is shown that reaching $T_k$ cannot occur, and that the entropy only decreases to zero as $T \to 0$.

Figure 1.3 | Extrapolation of the entropy of the supercooled results in the Kauzmann entropy crisis: zero entropy at non-zero temperature. Figure drawn from Ref. [30].

Dynamical heterogeneities are the fourth key phenomena of supercooled liquids and are qualitatively illustrated in Figure 1.4. First predicted by Adam and Gibbs in 1965 [44], the concept has only become widely accepted in the past two decades as a result of numerous exceptional experimental and simulation results [31,45–48]. In brief, relaxation measurements routinely result in a broad distribution of relaxation times, leading to the conclusion that relaxation dynamics must be heterogeneous. Results on colloidal and other granular materials [49–53] reveal dynamic heterogeneities in simpler systems, and their similarity [54] to glassy materials provides an analog to understand the dynamics of the supercooled liquid. The role of structure and thermodynamics in dynamic heterogeneities is less clear, and multiple avenues of research are ongoing. For example, questions about the changing length scale of heterogeneous dynamics with temperature, the structural nature of the regions, and the energy barriers that give rise to this heterogeneity remain open.
Figure 1.4 | An illustration of dynamic heterogeneities over the duration of \( \tau_\alpha \) in a 2D Lenard-Jones mixture. Figure drawn from Ref. [48].

1.3 The Potential Energy Landscape

Glasses are, by nature, metastable materials. They are kinetically trapped in energetic minima until thermal or mechanical energy allows them to overcome the activation barriers necessary to reach a new, potentially more stable, configuration. This idea was first proposed by Goldstein [55] in 1969 and was termed the potential energy landscape (PEL). More formally, the PEL is a temperature-independent energetic description of a material as a function of its configuration space. While the PEL is often drawn conceptually in two dimensions, the dimensionality of the space is given by \( 3 \times (N - 1) \) where \( N \) is the number of particles in the system. The PEL of any material consists of energetic maxima and minima (often called basins and wells) as a function of its atomic positions. At low temperatures, a supercooled liquid or glass is trapped in a basin and its motion is dominated by the harmonic nature of its local topology, oscillating around a so-called inherent structure configuration at the energetic minima of the basin. Energetic activation via thermal fluctuations can lead to “aging” of the glass as it slowly traverses its PEL and explores new, lower minima.
The topology of a glass’s PEL is correlated with its formation and properties [56–64], but modeling and exploring the PEL has proven to be a daunting task. Stillinger and Weber [65] first introduced the idea of basins and inherent structures in 1982, forming the basis for a thermodynamic formalism of glass. Stillinger, Debenetti, Sastry, and co-authors [26,57,62,63,66–69] expanded on the theory developed by Stillinger and Weber in an exploration of the glass transition, relaxation phenomena, and dynamics. Wales [70] provided insight into the connections between barrier heights, path lengths, and vibrational frequencies that further constrain the PEL topology for real systems. Heuer [59,61,71] used simulation methods to explore the PEL and transport phenomena between metabasins (i.e. collections of many minima), providing a convincing argument for the existence of a low-energy cutoff of inherent structures in amorphous silica and illustrating both the avoidance of the Kauzmann entropy crisis and a crossover from fragile-to-strong behavior [72]. In order to overcome the computational infeasibility of exploring the PEL, the activation-relaxation technique was developed by Mousseau and Barkema [73]. The activation-relaxation technique identifies and traverses saddle points in the PEL to find new local minima, providing a mechanism for prioritizing changes in atomic configuration that sample different inherent structures. One critique of the PEL picture is that it necessitates a thermodynamic isochoric environment, whereas most experiments take place under isobaric conditions. Therefore the idea of an enthalpy landscape has been more recently developed to enumerate the thermodynamic differences between a volume-constrained and pressure-constrained environment [43,64,74–78]. Recent review articles [43,59,79,80] provide more information about the current state of the PEL and its role in glassy physics.

1.4 Dynamics in Glasses and Supercooled Liquids

As the supercooled liquid is cooled towards the glass transition, the change in viscosity follows either Arrhenius or super-Arrhenius behavior [81]. Strong glasses (e.g. silica
are those whose motion slows Arrheniusly, while \textit{fragile} glasses (e.g. o-terphenyl [82]) slow down super-Arrheniusly. The strong vs. fragile nature of a glass is measured by its fragility,

\[ m = \left[ \frac{d \log \tau(T)}{d(T_g/T)} \right]_{T \to T_g} = \left[ \frac{d \log n(T)}{d(T_g/T)} \right]_{T \to T_g}. \]

Fragility is fundamentally governed by the activation barriers in the PEL [26]. If barrier heights decrease with decreasing temperature, the glass is fragile and its structure is more amendable to changes during cooling or heating; this is why fragile glasses are often governed by Van der Waals forces rather than covalent bonding. On the other hand, strong glasses have nearly constant activation energy as a function of temperature, are less sensitive to small changes in atomic environment, and tend to have covalent bonding [84].

The dynamics of hopping over barriers on the PEL is often discussed in terms of relaxation times. Traversing large barriers between metabasins is correlated with the slow $\alpha$-relaxation, while jumps over small energy barriers within a metabasin are the result of the faster $\beta$-relaxations. Within this regime, $\beta$-relaxation is broken down into two separate phenomena: faster motions correlate with vibrational cage rattling effects, whereas the slowest $\beta$-relaxation is distinguished by the name Johari-Goldstein (JG) relaxation and is the result of bond swapping between nearest-neighbors [39]. Multiple JG relaxations provide short jumps between basins, an accumulation of which can result in one $\alpha$-relaxation [85]. Structurally, this implies that atoms move distances on the order of one nearest neighbor distance by a sequence of bond swaps between neighbors.

As the supercooled liquid approaches $T_g$, the $\alpha$-relaxation dies out as structural rearrangement can no longer be seen on experimental timescales. Once quenched into a glass, the $\alpha$-relaxation is only visible during aging. While aging, irreversible structural relaxations occur due
to thermal fluctuations and the slow traversal of the PEL. β-relaxations, on the other hand, persist into the glassy state—albeit at lower frequency—and are reversible processes.

While a universal theory for the physics of relaxation phenomena in supercooled liquids and glasses has not yet been developed, mode coupling theory (MCT) and random first-order transition theory (RFOT) provide insights into the glass transition. MCT [86] is derived from a dynamical basis, using density fluctuations as the foundation for its predictions. RFOT [87], on the other hand, relies on mean-field theory and statistical ensembles to model the glass transition. Both models use the Vogel-Fulcher-Tammann (VFT) equation

\[ \tau(T) = \tau_0 \exp \left( \frac{A}{T - T_0} \right) \]

(where \( \tau_0, A, \) and \( T_0 \) are fitting parameters) to predict a singularity reminiscent of the Kauzmann temperature when \( T = T_0 \). While the VFT equation has been used for decades to fit viscosity and relaxation data, the extrapolated value of \( T_k \) and the fit parameter \( T_0 \) often disagree. This has led to a more critical analysis of the VFT equation, usually via fragile glasses where a wide range of relaxation times exist in the supercooled liquid. The resulting discrepancies led the community to introduce new fitting functions for relaxation data that do not necessitate a temperature singularity [42,88–91]. Recent fits to relaxation and viscosity data have not led to an agreement regarding which functional form is correct [refs].

### 1.5 Glass Structure

The arrangement of atoms or molecules in the solid glassy state is the focus of studies on glass structure. Inherent structures with different atomic positions but indistinguishable properties, including thermodynamic properties such as enthalpy, can exist, meaning that the structure of a glass is not unique. This necessitates a statistical approach to the determination of all glass structures, focusing on structural features rather than exact atomic positions. Upon solidification,
the glass inherits some properties of the parent liquid, most importantly its lack of long-range order and amorphous character.

Structure studies of glasses often use topological descriptors, spatial correlation functions and their Fourier analogs, or chemical properties to characterize the relative position of atoms or clusters of atoms. These metrics measure structure on multiple length scales. Short-range order (SRO) comprises the approximately Angstrom distance, usually incorporating a selection of atoms separated by a single bond length, while long-range order (LRO) is characterized by strong translational symmetry indicative of crystalline structure. Medium-range order (MRO) at the nanometer length scale falls between SRO and LRO and is often discussed in terms of the interactions of clusters of SRO units.

### 1.5.1 Short Range Order

SRO has been extensively measured by x-ray diffraction (XRD) and related techniques in many materials. SRO via XRD is characterized by the structure factor,

\[
S(k) = 1 + \frac{4\pi\rho}{k} \int_0^\infty r[g(r) - 1] \sin(kr) \, dr
\]

where \( k \) is the magnitude of the diffraction vector, \( \rho \) is the density, and \( r \) is the real-space distance between atoms. The real-space analog to \( S(k) \) is a pair-correlation function that measures the probability of finding an atom a distance \( r \) away from an arbitrary atom[92],

\[
g_2(r) = \frac{1}{4\pi r^2 \rho N} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \delta(r - |\mathbf{r}_{ij}|).
\]

In glasses, SRO characterized by \( g_2(r) \) is quantified by the position, width, and height of the first peak, corresponding to the first coordination shell in the material. Additional peaks correspond to order at longer length scales but the intensity eventually falls to zero due to the lack of LRO. \( g_2(r) \) can be broken down into a series of partial pair distribution functions for multicomponent systems.
These functions, often denoted \( g_{ij}^{ij}(r) \) where \( i \) and \( j \) are atomic species, calculate \( g_2(r) \) but only take into account species \( i \) and \( j \), resulting in information about the interatomic distances between different atomic species. The partial pair distribution functions are a measure of chemical order.

In simulations, structure at all lengths scales is directly accessible. Common techniques to characterize SRO include calculations of \( g_2(r) \), common neighbor analysis, Voronoi index analysis, and lower-order approximations such as coordination number, packing fraction, and atomic density. Common neighbor analysis (CNA) \([93]\) uses the nearest 2-6 atoms to characterize the local topology of an atom’s environment. While it is an excellent indicator of structure for materials with a low average coordination number, in systems such as MGs where coordination numbers can range from 8-16, CNA lacks the necessary granularity. The Voronoi tessellation technique \([94]\) is one solution to this problem. It is the real-space analog of the first Brillouin zone, constructed by considering the interior volume of the perpendicular bisecting planes to the atom-to-atom position vectors. It is considered to be the volume that “belongs to” an atom. Because of the large coordination numbers for MGs, the resulting Voronoi polyhedra are complex. The lower order approximation techniques are averages and compress multidimensional information into one (or a few) numbers. While trends do exist as a function of composition or preparation methods, these averages are often insufficient to predict material properties.

Oxide glasses are the exemplar for successful design via SRO. Topological constraint theory has played a large part in this success, allowing quantitative prediction of glass properties by balancing the number of atomic degrees of freedom with the number of interatomic force field constraints \([95]\). The ground work for topological constraint theory was set by Zachariasen \([14]\) in 1932 and developed further by Gupta and Cooper \([96,97]\) and Phillips and Thorpe \([98,99]\). Recent work has been summarized by Mauro \([76]\) and Smedskjaer \([43]\) as well as Micoulaut and Popescu \([100]\) and includes the practical applications of topological constraint theory. By optimizing the
rigidity of a glassy network via balance stretching vs. bending constraints, ideal compositions can be found. For example, increasing the network modifier cation concentration in silicate glasses increases the number of non-bridging oxygens and decreases network rigidity. Too few cations will result in an over-constrained, stressed glass, whereas too many cations will result in an under-constrained, floppy network. As a spectacular example, balancing these constraints led to the prediction of the optimal composition of window glass [101].

1.5.2 Medium Range Order

While the successes of SRO analyses have played an important role in network forming glasses in particular, MRO is believed to be crucial in determining many properties of glasses [102–109]. Higher-order correlation functions can be used to probe this interatomic ordering beyond pair interactions. Unfortunately, few experimentally observable correlations functions beyond $g_2(r)$ exist for amorphous materials. As a result, identification of MRO in glasses has largely been studied via simulations where exact atomic positions are readily available. One consistently reported feature of MRO that has been found in silica [108,110,111], 2D colloids [104], Lenard-Jones mixtures [36,112], and MG [113] is of crystal-like character. Four- and six-fold symmetry of SRO identified via Voronoi tessellation or correlation functions gives rise to locally connected—and highly distorted—crystal-like structure. Experimental evidence of this MRO has also been measured in some systems (colloid [114], MG [113], silica [111]) and these structures are believed to be linked to slow dynamics in simulations of some colloids [115]. Other MRO structures are typically system dependent, and those for MG are discussed in the following chapter.
1.6 Metallic Glass Structure

While MGs have the general properties of glasses, their metallic bonding characteristics make them interesting materials from both a theoretical and application standpoint. The lack of orientational order allows for a first-order approximation of their structure and properties simply from the chemical information of their constituent elements. This has led to basic theories such as the dense random packing of hard spheres [116,117] as well as straightforward property predictions [13]. However, these theories quickly break down when studied closely or over a wide compositional range. Therefore, while the basic bonding and atomic character of MGs presents simplicity, the interaction between elemental species has proven to be a complex and interesting discussion.

MRO may be key to understanding this complex structure-property relationship, and some researchers believe that MRO has a direct connection to properties such as shear banding, plastic flow, dynamic heterogeneities, and fragility [104,118–120]. For example, shear bands are believed to be of approximately MRO size, and the heat generated during plastic flow may result in the formation of nearby nanocrystals. Those nanocrystals may mitigate further growth of the shear bands if they form at the growth front, so the intricate interaction of these MRO structures may be necessary to understand the mechanical properties of MGs. The physics behind the connection between MRO and dynamical properties is even less well understood, and simulations are only beginning to probe this connection [121,122]. One recent publication [122] identifies a connection between diffusivity and structure, where atomic transport tends to be concentrated within liquid-like regions between MRO structures.

In 2000, Inoue proposed three necessarily criteria for good GFA of MGs: 1) a multicomponent composition, 2) atomic size ratios greater than 12%, and 3) negative heats of mixing between components. Since then, many new criteria for good GFA have been proposed
with various degrees of success depending on the system to which they are applied. Some of the most commonly used include $T_{rg} = T_g/T_m$ [123,124], $\Delta T_x = T_x - T_g$ [123,125], and $\gamma = T_x/(T_g + T_l)$ [126,127] where $T_x$ is the crystallization temperature, $T_m$ is the melting temperature, and $T_l$ is the liquidus temperature. Unfortunately, no metric can reliably predict new bulk MGs (BMGs) over a wide range of compositions. Moreover, many compositions exhibit minor alloying effects [128] such that doping some elements into the host alloy drastically changes properties, while doping of other elements produces little to no change.

Following Inoue’s criteria, cluster packing models have been proposed including dense random packed models [116,129], the cluster packing model [130,131], and the quasi-equivalent clusters model [102]. Miracle’s work [130,131], for example, hypothesizes that SRO in MG in the form of solute-solvent interaction depends on an atomic size ratio $R^*$ between solute and solvent atoms. At particular optimal values of $R^*$ corresponding to particular compositions, solute atoms pack efficiently around solvent atoms in the first coordination shell. This is linked directly to GFA, with densely packed structures resulting in better glass formers. Miracle notes that values of $R^*$ from 0.6-1.4 (depending on the species) can form densely packed structures in MG. The Ma group [13,102,109,132,133] expanded on this formulation by studying MGs via reverse Monte Carlo (RMC) and molecular dynamics simulations. They found that distorted icosahedral order plays a dominant role in the slowing down of glassy dynamics in some MG systems, likely due to its low energy configuration [134] and lack of long-range periodicity. This, along with many other studies (see Ref. [13] for a detailed review), has led to the belief that icosahedral order is a key indicator of improved GFA. For example, Cheng et al. [109] found that small amounts of Al addition to the Zr-Cu system notably increase both icosahedral order and GFA. Interestingly, despite the high GFA in these glasses, a perfect icosahedron has 12 atoms in the first coordination shell that are 1.05x larger than the center atom, which violates Inoue’s criterion promoting components with
atomic size ratios greater than 12%. Additionally, Cheng et al. report that $R_{Zr}/R_{Al} = 1.05$ in Al-rich AlZr alloys, which have very poor GFA [135] in comparison to the ZrCuAl system. It is possible that the structurally preferred icosahedra compete with the preferred structures that arise due to high atomic size ratios, with different structures being optimal in different systems due to complicated chemical interactions [136]. This balance between geometrically efficient packing and chemical stability is poorly understood for MGs and seems to be system dependent.

Despite these complications, cluster packing models provide an avenue to connect the SRO of MG to MRO. By identifying connectivity of local units—for example via face, edge, or vertex sharing—structural connectivity on the MRO length scale can be characterized. Unfortunately there are few experimental techniques that can probe this type of information, and studies rely heavily on theoretical [130,131] and simulation methods [102,113] to access MRO structure in MGs. For example, molecular dynamics and RMC simulations indicate that string-like or backbone structures are key in metal-metal systems [102,113,137]. If this is true, the idea of an immobile backbone makes connections to percolation [138,139] and critical behavior [36] theories in which these structures immobilize the bulk structure during the glass transition. Other models of MRO focus on high symmetry structures, such as crystal-like MRO or non-crystal-like Bergman and Mackay clusters with symmetry out to the 3rd coordination shell [106,140]. These larger types of MRO are only beginning to be explored as advances in simulation and experimental techniques continue. Because MRO is believed to be strongly connected to properties of MGs, the questions surrounding these topics are some of the most important in glass theory. Better methods of MRO characterization are therefore crucial.
2 Metallic Glass Structure Analysis: Common Methods

SRO in MGs is comprised of an atom and its nearest neighbors, henceforth called a *cluster*. SRO balances efficient packing on one hand and chemical ordering on the other [141]. Efficient packing of SRO clusters without long-range translational symmetry requires the structure of the material to be disrupted, and therefore identifying the structural units that cause this disruption and lack of connectivity at the short-range length scale is of considerable interest. The following techniques are typically used to study MG structure.

2.1 Molecular Dynamics

Molecular dynamics (MD) is an algorithm for simulating the positions and movements of atoms under the direction of a force field. Force fields in MD are approximated using empirical interaction potentials that govern the interatomic interactions. The atoms are modeled as single-point particles with a mass and charge. Given a configuration of atom positions and velocities, the new position of each atom is calculated using information from the force field and the velocity of the atom according to Newton’s equation of motion: \( m_i \ddot{r}_i = \sum_{j \neq i} F_{ij} \) where \( m_i \) is the mass and \( \ddot{r}_i \) is the acceleration of atom \( i \) and \( F_{ij} \) is the force between atom \( i \) and atom \( j \). Under the assumption of constant acceleration, Newton’s equation of motion can be integrated using the Velocity-Verlet approximation [142] to derive the following equations for the updated position and velocity of each atom:

\[
\begin{align*}
  r_i(t + dt) &= r_i(t) + v_i(t)dt + \frac{1}{2} \frac{F_i(t)}{m_i}(dt)^2 \\
  v_i(t + dt) &= v_i(t) + \frac{F_i(t) + F_i(t + dt)}{2m}dt
\end{align*}
\]
where $F_i$ is the total force acting on atom $i$ and $dt$ is a finite time (the timestep), typically on the order of 1 fs. Smaller values of $dt$ increase the accuracy of the updated position and velocity approximations at the cost of higher computational cost, and vice versa.

Molecular dynamics simulations in the context of MG synthesis [13] typically quench a liquid composition at a cooling rate of $10^{12}$ to $10^9$ K/s. Lower cooling rates allow the supercooled liquid to remain in equilibrium down to lower temperatures, resulting in a lower energy glass when the supercooled liquid falls out of equilibrium into the glassy state. An isothermal-isobaric ensemble (NPT) is typically used during the quench and the temperature of the system is decreased in increments which holding at approximately zero pressure and constant composition and number of atoms.

2.2 Conjugate Gradient Minimization

Conjugate Gradient minimization (CGM) is analogous to MD in that it simulates the positions of atoms under the direction of an empirical interaction potential. CGM, however, ignores the velocity of the atoms and instead relaxes the atom configuration into the nearest local energy minimum by considering only the interatomic forces defined by the potential. Performing a CGM on a MG configuration “relaxes” the configuration into its nearest local energy minimum, and the resulting structure is called the glass configuration’s inherent structure. Glass configurations that are similar but not identical (e.g. a few atom positions are a fraction of an angstrom different) likely have the same inherent structure. The concept of an amorphous material’s inherent structures provides a few useful simplifications. Namely, an amorphous material has a finite number of inherent structures, two atomic configurations can be considered “similar” if they have the same inherent structure, and the kinetics that result from atomic velocities can be ignored which results in more precise atomic positions that can be used to draw correlations with properties.
2.3 Voronoi Analysis

Voronoi tessellation is a geometrical decomposition of the material structure and serves as an alternative representation of the structure. The Voronoi tessellation method is reversible, meaning that in addition to being able to calculate the Voronoi tessellation from the atom coordinates, one can also calculate the atom coordinates from the Voronoi tessellation. The geometrical Voronoi tessellation technique becomes topological when the polyhedra in the tessellation are abstracted into a set of integers describing the shape of the polyhedra. In particular, when analyzing the local structure around an atom, Voronoi tessellation uses the nearest-neighbor atoms to generate a polygon around the center atom and the polygon is abstracted into a set of integers, \(<n_3, n_4, n_5, n_6, ...>\), designating the number of faces in the polygon with 3, 4, 5, 6, … faces.

This Voronoi index (VI) [143] analysis is the most common approach to analyzing the structure of atomistic models of MGs. Qualitatively, VI analysis abstracts the exact atomic positions of SRO units into shapes and describes those shapes qualitatively and independent of orientation. In this formalism, a polygon is constructed that represents the volume that “belongs to” an atom, in the sense that every point in the volume is closer to the central atom than to any other atom in the structure. Because of the large coordination numbers of MGs, their Voronoi polyhedra are complex. The VIs are used as a characterization of the atom’s local environment. VI analysis enables a binary metric of similarity for the local structure around two atoms (i.e. do these two atoms have the same VI, yes or no?).

Unfortunately, VIs have little intuitive meaning and are sensitive to small variations in atom positions under some circumstances. Figure S3 in Ref. [102] illustrates these points: an insignificant change in atom position changes the VI, and the indices themselves do not lend themselves to an intuitive understanding of the underlying SRO structure they represent. Despite
this issue, VIs allow for an abstract description of an atom’s local environment independent of position and orientation.

2.4 Methods Parameters

Unless otherwise noted the MD simulations in this work were performed with the purpose of cooling an alloy from a liquid state into a solid (glassy) state, with periodic boundary conditions applied to a cubic box, a 1 fs timestep, Nose-Hoover thermostat and barostat, and in an NPT ensemble. Potentials such as the embedded-atom model (EAM) or Finnis-Sinclair (EAM-FS) were used to approximate the interatomic interactions and MD and CGM calculations were carried out using the simulation package LAMMPS [144].
3 Metallic Glass Structure Analysis: Unique Methods and New Developments

The computational timescales of MD simulations are often orders of magnitude smaller than timescales in experiments. For example, MD simulations of MD structures with a few thousand atoms are typically capped at cooling rates of \(10^{12}\) to \(10^9\) K/s while typical experimental cooling rates range from \(10^6\) to \(10^3\) K/s. The orders-of-magnitude faster cooling rates in MD simulations result in simulated structure of MGs that do not match experimental results [113,145–148]. This discrepancy motivates the use and creation of unique methods to generate MG structures with characteristics that are consistent with available experimental data (Chapters 3.4 and 3.5). Experimental techniques that measure MRO are uncommon. One such technique, fluctuation electron microscopy, is introduced in Chapter 3.1.

Topological descriptors have had great success as abstract descriptions of the structure of disordered materials. Topological descriptors are often derived from a connectivity graph with atoms as vertices and atomic bonds as edges. The connectivity graph preserves the topology of the structure but abandons the atomic coordinates. Various topological descriptors are derived from the connectivity graph, which differ in the structural length scale they describe. For example, CNA, which is highly localized, produces a triplet of integers that describes the topology of two atoms and their joint neighboring atoms [93]. VI analyses [149] are less localized than CNA and describe the topology of an atom and all of its nearest neighbors, typically 9-16 atoms in MG systems.

While VI and other topological structure analysis methods have proven useful, they discard information about the relative positions of atoms. Their topological nature is a benefit, since it confers a level of abstraction that has limited sensitivity to the details of atomic positions and rotations, but also a hindrance, since it is precisely the details of the atom positions that determine the strength of the interatomic interactions. Structure analysis methods that are based in geometry rather than topology and account for the rotational and translational difference in atom positions
between clusters may alleviate the difficulties of topological analysis techniques. Such a technique is discussed in Chapter 3.6.

3.1 Fluctuation Electron Microscopy

FEM [105,150–153] is one of the few experimental techniques that provides access to MRO in amorphous materials. However, the ability to probe this length scale comes at the cost of complexity. Transmission electron microscopy (TEM) images of amorphous materials suffer from the 2D projection problem [154,155], making determination of the 3D structure difficult, and can be qualitatively reproduced by applying a band pass filter to random noise [105]. The deviation from this Gaussian noise distribution in the image is the quantitative signal of non-random structure information in amorphous samples. FEM builds up significant deviations by statistical analysis of a large number of images, on the order of one thousand per sample.

FEM measures the variance of the diffracted intensity arising from a material’s structure, which depends on two-, three-, and four-body correlation functions [152]. Figure 3.1 illustrates the process of acquiring FEM data. A coherent probe is focused on the sample and nanodiffraction patterns are recorded via scanning TEM (STEM). After collecting hundreds or thousands of patterns, each pattern is azimuthally integrated to calculate the variance of the dataset, $V(k)$. $V(k)$ is a measure of structural heterogeneity, and the coherent constructive and destructive interference associated with diffraction from ordered structures provides the crucial diffraction information [151]. $V(k)$ is defined as

$$V(k) = \frac{\langle I^2(k,r) \rangle}{\langle I(k,r) \rangle^2}$$

where $\langle \rangle$ indicates averaging over the position, $r$, on the sample, $k$ is the scattering vector magnitude, and $I$ is the diffracted intensity.
Figure 3.1 | FEM in a STEM. Nanodiffraction patterns are collected by scanning a nanometer-sized probe across the sample. The mean and variance of the patterns are then calculated as a measure of MRO. Figure drawn from Ref. [105].

3.2 3D Fourier Transform

Improvements to a reciprocal space method were developed [146] to visualize and analyze the structure of atomic models in reciprocal space. This analysis technique is complementary to data from FEM measurements because FEM is a diffraction technique and the structure it imposes on atomic models derived from that data is well-visualized in reciprocal space. An fcc aluminum crystal inside a larger box illustrates this process in Figure 3.2. First, the model is transformed into reciprocal space (Figure 3.2b) via a three-dimensional Fourier transform (FT),

$$S(k) = \sum_n f_n(|k|)e^{2\pi i k \cdot r_n},$$

where $f_n$ is the atomic scattering factor for atom $n$, $k$ is the wavevector, and $r_n$ is atom $n$’s position. The complex vector $S(k)$ is not accessible in conventional experiments which only measure the real part of the function after isotropic averaging to yield $|S(k)|$. High intensity spots in the 3D FT are found using conventional feature analysis techniques implemented in Python or Igor Pro software, and fitting to an asymmetric 3D Gaussian refines their positions and size. The functional form of an asymmetric 3D Gaussian is given by
\[ G(x, y, z) = \exp\left[ \frac{1}{2}(1 - c_{xy}^2 - c_{xz}^2 - c_{yz}^2 + 2c_{xy}c_{xz}c_{yz})^{-1} \right] \]

\[ \sum_{i,j,k=x,y,z} (c_{ij}^2 - 1) \frac{(k - k_0)^2}{\sigma_k^2} + \frac{2(i - i_0)(j - j_0)(c_{ij} - c_{ik}c_{jk})}{\sigma_i \sigma_j} \]

where the summation over \( i,j,k = x,y,z \) indicates cycling through the index order.

To connect reciprocal space back to real space, we use Fourier filtering. A Gaussian windowing function is applied to the spot \( g \) and its symmetric reflection \(-g\), filtering out all other diffraction phenomena (Figure 3.2b). The filtered 3D image is back-transformed into real space (Figure 3.2c) via

\[ |F(r)| = \sum_k |S(k) e^{-2\pi i k \cdot r}|. \]

\( |F(r)| \) is a continuous function describing the electron scattering power of the sample, analogous to the electron density map obtained in x-ray crystallography. The result of the windowed back transform is a set of fringes perpendicular to \( g \), with periodicity \( 2/|g| \). The amplitude of the fringes is highest in the region of the model that contains atoms separated by \( 2/|g| \), so smoothing the back transforms highlights that chapter of the model (Figure 3.2d). This method is applied to the 3D structures of various HRMC models in this work and identifies the MRO structures that give rise to particular features in \( V(k) \). This method enables the connection of specific features in \( V(k) \) with MRO atomic structures in the model.
Figure 3.2 | All images are 2D projections of 3D images. a) An aluminum fcc nanocrystal inside a larger box; b) FT of model in (a) with a (111) spot selected for filtering (the symmetric reflection, also selected, is in a different plane); c) IFT of the selected spot in (b) (and its symmetric reflection); d) image (c) after smoothing overlaid with the original model position.

3.3 An Introduction to Reverse Structure Determination

The determination of the atomic structure of materials is a ubiquitous problem in materials science [156]. Crystals with large unit cells, amorphous materials, and interfaces often have complex structure-property relationships that necessitate a thorough understanding of the material’s atomic structure. In a typical approach to complex structure determination, a researcher would combine available data from experiments and simulations using scientific intuition, prior knowledge, and trial-and-error to discover the “best” structure for a given material. “Best” is often defined as the lowest energy structure most consistent with experimental data subject to (sometimes vague) constraints from prior knowledge. Unfortunately, available experimental data typically lack the information necessary to uniquely determine three-dimensional (3D) structure information, particularly for complex structures such as MGs. Pure simulation approaches, on the other hand, must often make approximations to reach realistic length and time scales at atomic resolution and therefore often cannot model realistic conditions giving rise to metastable structures or structures stabilized by complex environmental factors. Combining experimental data with
simulations can provide the necessary spatio-temporal resolution and scale for systematic structure determination and allow structures to be determined that minimize energy as much as possible while remaining consistent with available experimental data.

Reverse structure determination algorithms iteratively refine an atomic model by modifying the structure—for example by changing the positions of atoms—until the structure minimizes an objective function based on experimental data. This problem can be formulated mathematically using an atomic configuration \( \theta \) by defining an objective function

\[
O(\theta) = \sum_{i}^{N} \alpha_i f_i(\theta, D, C),
\]

with the goal of minimizing \( O(\theta) \) by iteratively updating the atomic configuration. \( f_i \) are specific terms of the objective function that evaluate a specific property of \( \theta \). For any given application, at least one \( f_i \) is likely to be an evaluation of energy. Additional \( f_i \) can be defined that are related to experimental data \( D \) or user specified structural constraints \( C \). \( \alpha_i \) are weighting factors chosen to give a desired numerical importance to each component of the objective function, typically set so that different contributions make similar levels of contributions to \( O(\theta) \). Any number of terms can be included in the objective function. Other multi-objective optimization schemes exist that remove the need to explicitly set each \( \alpha_i \) (such as Bayesian [157] and Pareto front [158] optimization), although these involve greater code and operation complexity and sometimes higher computation expense. For the remainder of this dissertation, the individual objective function terms will be referred to as *fitness functions* and their numerical output is as *fitness scores*.

In this work, two approaches are used to minimize \( O(\theta) \) to obtain atomic structure(s) with low values of each term in \( O(\theta) \). Hybrid reverse Monte Carlo (HRMC) was used to identify MRO structure in Zr-Cu-Al, [159] and Pd-Si, and Al-Sm MGs, and StructOpt [156] shows promise for similar results at a fraction of the computational cost. The HRMC approach is based on simple
movements of a single atom at a time, while the second approach uses a genetic algorithm to update
the atomic positions in $\theta$ using more complicated algorithms. While HRMC works well for small
systems, its method of single-atom moves is prohibitively slow for larger models where the number
of atoms approaches 10,000. Larger models are interesting, however, because they are better suited
to study structure-property correlations beyond the SRO length scale. StructOpt solves this issue
with its genetic algorithm optimizer which replaces single atom moves with complex crossovers
and mutations, enabling faster exploration of the configuration space and potential energy
landscape. While StructOpt is still being tested, it shows promise for identifying MG structure at
a fraction of the computational cost of HRMC.

3.4 Hybrid Reverse Monte Carlo

Structures of various MG samples in this work were generated using hybrid-reverse Monte
Carlo (HRMC) simulations [111,160–162]. The HRMC simulations are constrained at the SRO
length scale by an empirical interatomic potential and at the MRO length scale by FEM data. The
HRMC algorithm uses Metropolis Monte Carlo with random single-atom moves to minimize the
objective function $O(\theta)_{HRMC} = \alpha \chi^2 + E$, were $E$ is the system potential energy, and $\chi^2$ measures
the discrepancy between the simulated variance $V_s(k)$ and the experimental variance $V(k)$. $\chi^2$ is
defined by

$$\chi^2 = \sum_l \left[ \frac{V(k_l) - \beta \cdot V_s(k_l)}{\sigma_{err}} \right]^2,$$

where $\sigma_{err}$ is the experimental error for each $V(k)$ data point and $\alpha$ is a weighting factor set to
encourage energy minimization while constraining the fit of the experimental data within
reasonable values (based on the experimental error). $\beta = \frac{1}{3} \frac{t_{sim}}{t_{exp}}$ is a scaling factor that corrects for
the thickness difference between the sample and the model and for the approximations in the $V(k)$
calculation [113,163].
HRMC simulations calculate the intensity of the FEM measurement $I(k)$ using the Dash et al. method [163]. To obtain enough samples from which to calculate $V$, $I$ is calculated with the incident electron beam traveling along 211 different directions, evenly spaced in solid angle on the top half of the unit circle. This approach is equivalent to duplicating the model many times with random rotations to make a larger structure, and it helps enforce orientational isotropy on the final structure. In the simulation, the pixels (which model the electron beam) are modified from circular in shape to square, and the model size $s$ is set by the experimental resolution $R$ by $s = \sqrt{2}R$ ($R = 2$ nm in this work). The combination of square pixels and the model size ensures each atom in the model contributes once and only once to the $I(k)$ calculation in each orientation.

The simulation minimizes the objective function using random, single-atom moves accepted or rejected according to the Metropolis algorithm and an effective temperature. The temperature is decreased in a simulated annealing framework after the objective function has equilibrated at a given temperature. The result is typically a model that is close in energy to the MD quenched glass and also in excellent agreement with the experimental FEM data. Minimizing the objective function requires $\sim 10^7$ random moves, which, using 64 cores on modern hardware, takes approximately five days to complete.

HRMC’s Metropolis algorithm accepts a random, single-atom move if the evaluation of the $O(\theta)_{HRMC}$ as a result of that move satisfies $\Delta O < 0$ or \( \text{rand} < \exp \left( -\frac{\Delta CF}{k_B T} \right) \), where $k_B$ is Boltzmann’s constant, $T$ is the system temperature, $\Delta O$ is the change in the CF’s value from the previous step to the current one, and \( \text{rand} \) is a random number in the range [0,1). Qualitatively, moves are accepted when the value of the objective function is either improved or worsened by an acceptable amount, as determined by the fictitious temperature, $T$. Higher values of $T$ will result in the acceptance of more poor moves, analogous to moving up the PEL during a purely energy-
constrained simulation. During HRMC, $T$ is decreased exponentially via a simulated annealing approach to allow for convergence of the simulation.

The part of HRMC that simulates the FEM data is called FEMSIM. The general outline of the pseudocode is as follows:

1. load an atomic model;
2. create a series of rotated models by rotating the input from (1) through different Euler angles distributed symmetrically about the unit sphere (~ 200 unique rotations were used in this work);
3. and calculate $V(k)$ via the Dash, et. al. method [163] using the rotated models from (2) as different pixel positions.

The value of $\alpha$ is set to ensure that changes in $E$ and $\chi^2$ affect the objective function to a similar degree. For example, while the average change in $E$ may be of the order $10^{-3}$ eV, changes in $\chi^2$ are dependent on the experiment and can therefore be significantly larger or smaller numerically. In practice, these changes in $E$ and $\chi^2$ change over the course of the simulation. Therefore, only the final convergence state of the simulation was taken into consideration, at which point the energy and the weighted fit to the data should be numerically similar. For the simulations in this work an increase in energy of ~ 0.0256 eV/atom was allowed for between a model equilibrated at room temperature via MD and the HRMC equilibrated model. HRMC models are expected to have higher energies than MD or pure MC due to the competition of the energetic and experimental constraints [164]. Given an acceptable “error” in energy of 0.0256 eV/atom at the completion of the simulation, $\chi^2$ should be similar to $E$. Simplifying $\frac{\alpha \chi^2}{E} = 0.0256$ with $\chi^2 \approx E$ yields $\alpha = 0.0256$. This result was used for the majority of the simulations in this work.

MD simulations in an NPT ensemble at zero pressure were used to determine the equilibrium densities of the glassy states at room temperature, as predicted by the potential. A
2.83³ nm³ box was then randomly filled with atoms with the same atom density and correct alloy composition, and CGM in LAMMPS was used to find a local minimum of the energy of the structure. The resulting dense random packed structure was used as the initial configuration for the HRMC simulations in this work.

3.5 **StructOpt**

StructOpt [156] is an open-source structure optimization suite that applies genetic algorithm and particle swarm methods to obtain atomic structures that minimize an objective function. The objective function typically consists of the energy and the error between simulated and experimental data, which is typically applied to determine structures that minimize energy to the extent possible while also being fully consistent with available experimental data. Two examples are presented: the structure of a metastable Pt nanoparticle is determined from energetic and scanning transmission electron microscopy data, and the structure of an amorphous-nanocrystal composite is determined from energetic and fluctuation electron microscopy data. StructOpt is modular in its construction and therefore is naturally extensible to include new materials simulation modules or new optimization methods, either written by the user or existing in other code packages. It uses the Message Passing Interface’s (MPI) dynamic process management functionality to allocate resources to computationally expensive codes on the fly, enabling StructOpt to take full advantage of the parallelization tools available in many scientific packages. StructOpt was developed in collaboration with Zhongnan Xu, Zhewen Song, Min Yu, Tam Mayeshiba, Dane Morgan, and Paul M. Voyles.

3.5.1 **StructOpt Overview**

StructOpt supports two structure determination algorithms: a genetic algorithm [165] and a particle swarm optimization [166,167]. Both algorithms are population-based optimization
schemes, allowing the features of the best candidate structures to collectively inform the creation of new candidates. These approaches allow for a more comprehensive search of the domain space given a sparse and diverse sampling of the initial population [165] than optimization approaches that operate on a single atomic structure such as HRMC. The particle swarm optimization implemented in StructOpt was generally found to be slower and less adept at finding deep minima in energy-only optimizations than the genetic algorithm, so the genetic algorithm is the focus in this work.

StructOpt supports optimization of atomic structures with periodic or non-periodic boundary conditions. Other constraints can be readily added due to the modular structure of the code. These constraints can help to define the type of structure that can be realized, such as nanoclusters with 3D surfaces, amorphous materials with or without periodic boundary conditions, and crystals with various symmetry constraints. All the operations within StructOpt can be applied to any type of structure, although some operations are more useful for one structure type than another. For example, an operation that moves surface atoms on a nanocluster may not have any surfaces on which to apply this move for a structure with periodic boundary conditions in all directions. The constraints on the structure can be defined by the user and can be as simple or complicated as the nature of the problem requires.

StructOpt defines a set of operations that can be applied to specific structures. In the context of genetic algorithms, these include crossovers, mutations, relaxations, and fitnesses. After creating or loading a set of atomic structures, the genetic algorithm performs crossovers on the population. Crossovers combine two structures by patching them together in unique ways, and result in two new structures that are added to the population. StructOpt then performs mutations on a subset of the population’s structures, which modify a single structure to create a single new structure. Because crossovers and mutations can create unstable structures, relaxations are
performed to move the atomic configuration towards a local minimum of one or more parts of the objective function (for example, some relaxations are designed to bring the modified structures into energetic equilibrium). Fitness evaluations require forward simulations performed on a static structure and provide information about the “goodness” of the structure. Fitness evaluations are run after the relaxation process. The weighted sum of the fitness evaluations in Eq. 3.1 provides a single fitness score for each individual. Once all structures have been assigned a fitness score, StructOpt uses this information to remove certain structures from its current population and repeats the above processes. This iterative procedure is repeated until the convergence criteria—usually based on the fitness scores—are satisfied. StructOpt does not limit these operations (crossovers, mutations, relaxations, forward simulations, and structure selectors) to genetic algorithms, so they can be used within other optimization algorithms defined in StructOpt or defined by the user.

Crossovers and mutations modify the atomic structure to sample both nearby and distant parts of the configuration space. Given a diverse starting population, crossovers allow for sampling new areas of the search space by combining two distinct solutions, whereas mutations are perturbations on an existing structure. The crossovers implemented in StructOpt include a crossover that rotates two models, cuts both rotated models along a plane, and glues the opposing slices together, producing two children [168]. The mutations in StructOpt are numerous and include swapping atom species, randomly moving a single atom, randomly moving a cluster of atoms, moving atoms from the bulk to the surface, and twisting the model. Mutations and crossovers are among the simplest operations to add to StructOpt, and they can be configured to work differently on different structure types.

StructOpt implements three structural relaxation approaches, which are primarily used to relax locally unstable atomic configurations that result from crossovers, mutations, etc. The first is to relax energy using the molecular simulation package LAMMPS [144]. StructOpt can use any
minimization algorithm provided by LAMMPS to relax the atomic structure, including conjugate gradient minimization or molecular dynamics. The second relaxation mechanism is a hard-sphere relaxation that simply moves atoms to ensure that no two atoms overlap a fixed radius around each atom. Finally, StructOpt has implemented a special relaxation of atomic positions related to STEM image matching, which we call the “STEM relaxation”. The STEM relaxation performs a rotation of the atomic model to best match the STEM image without changing the positions of the atoms relative to one another.

StructOpt implements three objective function terms. The first term, called LAMMPS inside StructOpt, finds the potential energy of the relaxed atomic arrangement using the LAMMPS package which requires the user to choose an appropriate interatomic potential. The optimization of the LAMMPS objective function term attempts to find the lowest energy arrangement, and if it is the only term in the objective function it will ideally yield the zero-temperature ground state of the applied interatomic potential for the given constraints. The second routine, called STEMSIM, provides an algorithm for comparing atomic structures to STEM images. STEMSIM [169] calculates the discrepancy in pixel intensities between a STEM experimental image and a simple linear convolution STEM image simulation model [38,39]. If STEMSIM is the only term in the objective function, then the ideal optimized structure will have atom positions consistent with the experimental STEM image along one 2D orientation, but the bond lengths in other orientations and atomic forces and energies will be unconstrained and may be unrealistic. FEMSIM calculates the discrepancy between fluctuation electron microscopy (FEM) experimental data and a FEM simulation using a kinematic diffraction approach [163,171] and is useful for amorphous systems. Similar to STEMSIM, if FEMSIM is the only term in the objective function then the optimized structure will be consistent with the experimental data but may have unphysical atom positions which are very far from an energy minimum [172]. Examples of the use cases of these objective
terms can be found in the examples presented in Chapter 3.

After the objective functions of all individuals in the population are calculated, the final task of the genetic algorithm is deciding which individuals are discarded in the next generation. StructOpt includes selection and predator operations for choosing which individuals to mate and keep, respectively, by evaluating their objective function. StructOpt comes with several operators that affect the diversity of the population. Selection and predator operators such as “best”, “rank”, and “roulette” promote the dissemination and retention of the best individual’s features, while “fuss” and “tournament” have the option of maintaining a more diverse population [173–175]. Predators can also be used to eliminate duplicate structures, thereby increasing diversity and eliminating premature convergence on a non-ideal structure.

3.5.2 StructOpt Examples

Figures 3.3 compares the optimization of just the energy term with the optimization of both the energy and STEMSIM terms for refining the structure of nanoparticles. Figure 3.3 shows a similar comparison using the FEMSIM term and the structure of amorphous materials. In both cases, simulated data is substituted for experimental data for better model assessment. Such simulated data is often called phantom data because the structure that is used to create the data is known a priori. Therefore, the target of the optimization is also known a priori. When the simulation finishes, the output structure(s) can be compared to the target structure to quantitatively determine the accuracy of the solution(s).

In Figure 3.3(a), StructOpt optimized the structure of a 561 atom Pt nanoparticle (Pt$_{561}$) using an embedded-atom method (EAM) force field potential [176]. The initial population consisted of 18 randomly generated fcc particles already in the (100) orientation, and the STEMSIM relaxation procedure was used to align the modified atomic structures to the STEM image throughout the optimization. When the optimization was constrained by only the system
energy, StructOpt found the icosahedral Pt$_{561}$ particle, which is the lowest energy, magic number particle with 561 atoms [177,178]. The icosahedral structure is fcc-like with tilt boundaries that allow the surface to consist of low energy, hexagonal close-packed planes with a low surface-to-volume ratio. The final structure has minor surface defects with respect to the perfect icosahedral structure, but the overall icosahedral symmetry is found.

When a STEM fitness function is added to the objective function, StructOpt identifies a different, metastable optimal structure. In Figure 3.3(b), the objective function is modified to contain both an energetic term ($E_f$) and a term representing the fit ($\chi^2$) to a simulated STEM image of a 561 atom cuboctahedron. The cuboctahedron shape has an fcc structure with no defects and exposes higher energy (100) surfaces captured in the phantom STEM image which do not exist in the icosahedron in Figure 3.3(a). When the additional constraint of error vs. the phantom is added to the objective function (with $\alpha_{LAMMPS} = 1$ and $\alpha_{STEMSIM} = 100$), the Pt$_{561}$ icosahedron is not found as the optimal structure and instead StructOpt identifies the cuboctahedron as the correct target structure. Note that the experimental image is simulated, so the STEM fitness at the end of the algorithm has a fitness value close to zero upon finding the optimal structure. The fitness value is not exactly zero because the identified structure has minor surface defects with respect to the target structure, but previous results using this technique show that for phantom data the atom positions are recovered nearly exactly [179]. The optimization using STEM data only has not been carried out, since the STEM data will not constrain the structure in the direction perpendicular to the plane of the image. As a result, the optimized structure is guaranteed to be unphysical [172].

Figure 3.4 shows results for the optimization of 256 atoms of Al with periodic boundary conditions using an Al EAM potential [180]. Similar to Figure 3.3(a), the optimization shown in Figure 3.4(a) is performed with just an energy term. In this case the fcc Al ground state is obtained, as expected. The optimization in Figure 3.4(b) includes both energy and forward simulation
objective function terms, where the simulation is compared to phantom FEM data calculated from an amorphous/nanocrystal composite structure proposed as a model for high Al-content MGs [181] (See [182], Figure 1 for example experimental data on Al$_{88}$Y$_7$Fe$_5$). Since the target structure is a model of a glass, it is metastable in energy. The initial population for the genetic algorithm contained purely amorphous structures, and the crossovers and mutations modified the structures in the population until an amorphous-nanocrystal composite was formed that matched the experimental data well and had low energy. The FEM data captures the nanometer-scale order information of the phantom composite material, driving the optimal structure away from the energetically optimal fcc Al single crystal (Figure 3.4(a)) and towards a metastable material that has better agreement with the FEM data (Figure 3.4(b)). The fraction of VIs that are crystal-like [113] is similar in the final optimized structure and the phantom structure.
Figure 3.3 | A StructOpt run optimizing the structure of a Pt$_{561}$ nanoparticle using an EAM potential (a) without and (b) with the STEMSIM term in the objective function. The inset in (a) shows the Pt$_{561}$ regular icosahedron with 20-fold symmetry found by StructOpt using only an energy term in the objective function. The inset in (b)-upper shows the Pt$_{561}$ cuboctahedron refined by StructOpt using both energy and STEMSIM terms in the objective function. Minimization of the relative stability, $E_f$, drives the energy of the system down. Meanwhile, the STEMSIM term ($\chi^2$) gives the magnitude of the error between the forward STEMSIM simulation and the STEM image in inset (b)-lower, and drives the system toward agreement with the phantom experimental data. The blue and red dashed lines show the relative formation energies of the Pt$_{561}$ icosahedron and cuboctahedron particles, respectively, calculated using an EAM potential and LAMMPS.
Figure 3.4 | A StructOpt run optimizing the structure of Al using an EAM potential (a) without and (b) with the FEMSIM fitness function and phantom data from a nanocrystal/amorphous composite. The black lines show the fitness values calculated by StructOpt using LAMMPS and FEMSIM. The blue and red dashed lines show the formation energies of an Al fcc crystal and the nanocrystal/amorphous composite target, respectively, calculated using an EAM potential in LAMMPS. The inset in (a) shows the Al\textsubscript{256} fcc structure found with an energy-only optimization. The inset in (b)-upper shows an Al\textsubscript{3692} amorphous structure refined by StructOpt when the FEM data in inset (b)-lower is incorporated into the FEMSIM cost function. In the inset in (b)-lower, the blue line is the FEMSIM data of the phantom target and the green line is the FEMSIM data of the optimal structure StructOpt identified.

3.5.3 StructOpt Code Architecture

StructOpt is written in python and is open-source. It was designed with modularity and flexibility in mind, and its object-oriented approach makes clear distinctions between different types of functionality. The code has three important pieces of functionality, which are the Individual class, the Population class, and the optimization algorithm. The Individual class is a
stand-alone object containing an atomic structure with the necessary functionality to operate on itself. The Population class contains a list of Individual instances and provides functionality for operating on Individual instances. The optimization algorithm uses the functionality of the Population class to iteratively modify the underlying individuals. It is the job of the optimizer to shape the individuals in the population into a form that satisfies the convergence criteria. By making clear distinctions between these different pieces of functionality, each part of the code can be used and modified independently.

The Individual class extends the ASE.Atoms [183] class and implements methods to modify an instance of itself in the context of the implemented optimization algorithms. Specifically, an Individual can mutate, relax, and perform various fitness evaluations on itself in the context of the genetic algorithm and can perform analogous operations for particle swarm. StructOpt makes use of ASE’s LAMMPS calculator to calculate energies from LAMMPS and to encourage code reuse. Because different types of atomic structures exist, StructOpt implements different classes that inherit from the Individual class. Subclasses of Individual implement methods that are specific to the atomic structure they are modeling, overriding any necessary functionality. The two types of structures currently implemented in StructOpt are the Periodic and APeriodic classes which enforce and do not enforce periodic boundary conditions, respectively. Materials problems that require nanoclusters can use the APeriodic structure type, while materials problems that require optimizing unit-cells of crystals or supercells of more complex materials can use the Periodic structure type. Figure 3.4 is an example of using a Periodic structure to optimize an amorphous-nanocrystal composite. Implementing new Individual classes with different boundary conditions or other constraints only requires inheriting from the Individual and making any necessary physically-motivated modifications to the code. For example, a new Individual class might be called Surface, which would have periodic boundary conditions in two dimensions. Once defined,
the new Individual subclasses can be used immediately in any implemented optimization algorithm.

The Population class implements methods for operating on multiple Individual instances at once. For example, the Population can perform crossovers on and removals of the individuals in the population as required by the genetic algorithm. The Population also manages parallelized execution of the Individual methods. The complicating factor of this class is communication during parallelization because different parallelized processes can modify a Population instance in different ways. A more detailed description of the issues and implementation decisions around parallelization can be found in Chapter 6 and in the online documentation.

The goal of the optimization algorithm is to use the methods in the Population and Individual classes to modify the atomic structures into a form that satisfies the convergence criteria. Standard versions of genetic and particle swarm algorithms are included as examples, and users can modify these codes to apply additional optimization algorithms if desired.

StructOpt requires an input file specifying the details of the initial population, objective function terms, relaxation algorithms, output data, and parameters associated with the optimization algorithm, such as mutations, crossovers, and selection schemes for the genetic algorithm. These inputs parameterize the optimization and allow StructOpt to be highly configurable. This flexibility comes at the cost of increased complexity, so a hierarchical file format (json) was chosen to help mitigate some of the complexity. The output data of StructOpt simulations includes structure files, files for input/output of external programs such as LAMMPS, and logs of fitness scores, genealogy, and which crossovers/mutations were applied to specific atomic structures.

The output data can be parsed using a data exploration utility that is packaged with StructOpt called DataExplorer. In addition to providing standard data processing for reading outputs such as fitness scores, the data explorer provides utility functions for working with the
genealogy of the population after genetic algorithm optimization and provides access to all the functionality within StructOpt (e.g. relaxations, crossovers, and fitness calculations). Any operation that can be run on an Individual instance within StructOpt can also be applied to an atomic model loaded through the data explorer. It is therefore straightforward to reevaluate the fitness of a particular structure, for example, to identify a crucial turning point in the simulation. Additionally, since the data explorer is modularized in much the same way as the core components of StructOpt, its analysis techniques can be tied directly into StructOpt and used to tune the parameters of an optimization on-the-fly.

Finally, StructOpt also comes packaged with a simple job manager utility. This can be replaced by other workflow managers such as FireWorks [180], Pegasus [184], or CONDOR [185] but the built-in job manager provides a simple way to design a series of simulations and manage their results within a uniform environment. By combining the job manager with the data explorer, a single script can submit, track, and analyze a set of jobs for determining the behavior of the optimizer against various parameters. These capabilities are particularly useful for hyperparameter optimization, for example to test a variety of \( c \)'s in Eq 1 to determine their effect on the optimized structures.

### 3.5.4 Extending StructOpt Code

There are three areas in which the codebase is designed for easy modification and extension. New optimization algorithms can be implemented that use the current functionality in new ways; additional constraints can be implemented to cover a wider range of structure types; and new functionality for the optimizations (such as crossovers, fitnesses, etc.) can be added. Each of these areas of modifications can be done independently. For example, to add the particle swarm optimization to the existing code implementing genetic algorithms, we added a new module that updates the atomic positions via the approaches from the particle swarm method [186], which
replaced the genetic algorithm’s crossovers and mutations. The other functionality of StructOpt was used without modification. Smaller-scale modifications to the optimization scripts are also designed to be fast and intuitive to the user. For example, in a genetic algorithm optimization, the number of individuals in a population can be controlled by updating a parameter to the *Population.kill* method over the course of the simulation.

As an illustration of how to implement a new optimization constraint, consider the example of a crystal constrained to a specific space group. Atoms could be restricted to an asymmetric unit within the unit cell, then a set of symmetry operations could be implemented to extend those atoms to fill the unit cell or a large supercell if necessary. New mutations and crossovers could be defined to operate only on well-defined atom sites rather than general atom positions, and a short wrapper that populates the sites with atoms could be wrapped around the pre-existing *Individual* fitness and relaxation methods to easily incorporate their pre-existing functionality. Once crossovers, mutations, and wrapper functions have been written, the *Population* class and optimization algorithms can use this new constraint without modification to their code.

Finally, crossovers, mutations, and other methods that are designed to modify atomic structures in unique ways can be added easily. Each method is contained within its own file and is attached to the *Individual* class (or a subclass thereof) via an import in the corresponding file. Then, the new operations are enabled within the input file by specifying the name of the operation.

While StructOpt is written in Python, its functionality is not limited to Python. External programs that operate on atomic structures can be incorporated into StructOpt. In particular, the fitness modules in StructOpt are all implemented in different languages: STEMSIM is implemented in native Python; LAMMPS is written in C++; and FEMSIM is written in FORTRAN. Any relaxation code is expected to accept an atomic structure as input and output a
modified atomic structure. Similarly, any fitness operation is expected to accept an atomic structure and output a fitness score.

3.5.5 StructOpt Parallelization and Resource Allocation

In addition to being easily extensible, the code architecture allows for flexible resource management. Depending on the computational expense and complexity of the algorithm, the user can instruct StructOpt to allocate one or more cores to the methods that operate on the individuals in the population. For example, a force-field calculation of a system’s energy may require only one core, but a first-principles calculation may require many. The different computation algorithms and varying number of structures that need to be evaluated requires StructOpt to be capable of dynamically allocating its available resources at every iteration.

StructOpt utilizes two types of parallelization to handle resource allocation, shown schematically in Figure 3.5. The single-core-per-individual (SCPI) parallelization mechanism uses mpi4py [187–189] to distribute Individual instances over the available cores. If there are at least as many cores as Individual instances, each instance is assigned to a different core. If there are more Individual instances than cores, the instances will be divided amongst the available cores, and the instances that are assigned to the same core will be evaluated serially on that core. This method does not support parallelization to more cores than there are Individual instances. mpi4py handles the communication required to collect the updated information from each core and redistribute the updated Individual instances.
Figure 3.5 | The SCPI (a) and MPMD (b) methods differ in the way in which they parallelize the code. Standalone operations that are computationally expensive benefit from MPI’s MPMD functionality, while less computationally intensive operations can be parallelized at the population level using SCPI.

If an evaluation algorithm (such as FEMSIM) already takes advantage of MPI, it can be used within StructOpt via the multiple-program-multiple-data (MPMD) functionality supported by OpenMPI [190]. Under the MPMD settings, StructOpt uses the `MPI_Spawn_Multiple` command to allocate multiple cores to each *Individual* instance. When using MPMD, the user can specify a range of cores to be used for each evaluation. StructOpt attempts to intelligently assign a number of cores to each *Individual* instance to minimize the total computation time. For example, if the user specifies that an evaluation should use between 2 and 16 cores, and for a given iteration four individuals need to be evaluated, StructOpt will allocate four cores to each Individual; if, for another iteration, only one individual needs to be evaluated, StructOpt will allocate all 16 cores to that one individual.
On the other hand, some operations are fast enough that they should only be run on the master core. These operations are defined by StructOpt’s \texttt{@root} Python decorator, which provides simple syntax for broadcasting the result of the operation on the master core to all other cores. For operations that are parallelized, the \texttt{allgather} operation in StructOpt collects the updated \textit{Individuals} from each core, combines them into a single updated \textit{Population}, and propagates the updated \textit{Population} to all cores.

StructOpt’s parallelization mechanisms allow a variety of different algorithms to be incorporated into its framework without significantly reducing each algorithm’s parallelized potential. It is likely that the algorithms that will most benefit from parallelization will be relaxation or fitness algorithms that either intelligently move atoms or perform simulations of experiments. Users can integrate their pre-existing techniques and codes into StructOpt to solve their own unique structure determination problems.

Population-based optimization algorithms have the advantage that they can be highly parallelized. StructOpt takes advantage of this potential by combining both SCPI and MPMD parallelization schemes into a dynamic resource management system. SCPI and MPMD scale differently with the number of cores used. SCPI parallelizes up to a number of cores equal to the number of individuals in the population, while MPMD is limited by the scaling potential of the operation that is being parallelized (per individual). For example, assuming an MPMD program is efficient up to 100 cores and StructOpt uses a population size of 20, the code has the potential to scale up to \(20 \times 100 = 2,000\) cores. The limitation to scaling of this type is the time spent outside the parallelized MPMD functions, which will reduce the speedup of the overall code at a high number of cores, following Amdahl’s law. In addition, a combination of SCPI and MPMD processes may result in many cores being unused for a non-trivial amount of wall-clock time, in which case the scaling of StructOpt will be poor. In practice, we find that StructOpt parallelizes with a speedup
of 50-100% up to one core per individual for a range of problems. The speedup drops significantly at higher numbers of cores, but in a way that is strongly problem-specific.

3.5.6 StructOpt Summary

StructOpt, an open-source structure determination program, provides a framework for incorporating simulated energies and experimental characterization data into atomic structure optimization of materials. StructOpt is highly modular and can therefore easily integrate new types of experimental data, optimization algorithms, and optimization constraints into its infrastructure. StructOpt has already been used to solve complex nanoparticle and amorphous structure problems. It currently implements genetic algorithm and particle swarm optimizations, and can use LAMMPS, STEM, and FEM data within its objective function. In addition, StructOpt implements an advanced dynamic resource allocation system to take advantage of MPI functionality and existing parallelized applications for materials simulations.

3.6 Motif Extraction

A geometric approach used to categorize glass SRO units is presented in Ref. [191] that yields a quantitative metric of similarity between two structures. The ability to compute a degree of similarity, or structural distance, between two clusters (called SRO units in this chapter to avoid confusion with machine learning clustering terminology), along with atom positions that preserve geometry, solves the difficulties of VI analysis. Similarity information enables the application of tools based on metric spaces for additional analysis of MG structure. Here [192] density-based clustering [193], a machine learning method based on metric spaces, is applied to learn idealized, important SRO unit structures from atomistic models of MGs.

A geometric similarity metric comparing two SRO units necessitates a solution to the rotational variance of the SRO units in a MG structure. Recently, a technique called point-pattern
matching (PPM) [191] was adapted from the computer vision literature to the study of the 3D structure of materials. PPM works by aligning two sets of 3D points into as similar of an orientation and position as possible using an approximate rigid graph registration technique that can handle mild disorder between the two structures. After alignment, the similarity of the structures can be compared using any geometric metric. A similar structure analysis technique was developed by Fang et al. [140,194,195]. Their cluster alignment technique applies molecular dynamics with two potentials—one to constrain the bond distances within a SRO unit and the other to encourage alignment of atom positions in different SRO units—to collectively align a group of SRO units. The result of the cluster alignment method is a set of SRO units, all in similar orientation. Using this collective alignment, a probability density map describes the most probable atom positions of the aligned SRO units. The PPM approach differs by enabling fast alignment of any two structures, rather than a global alignment of many structures. The PPM method facilitates quantification of similarity between all pairs of SRO units in a material, independent of a collective alignment.

PPM is used in this work to quantify the similarity between all pairs of SRO units in multiple MG models. These dissimilarity scores function as the equivalent of a distance metric between two points in multidimensional structural configuration space, which is the data needed for machine learning clustering algorithms to cluster similar sets of SRO units. In this way, all of the important classes of SRO structures in the MG are learned directly from the atom position data, without human intervention.

The motif extraction method is illustrated in Figure 3.6. The nearest neighbors of each atom in an atomic model was identified using a radial cutoff corresponding to the minimum between the first and second peaks in the total pair distribution function (e.g. 3.6 Å for a Z\textsubscript{50}Cu\textsubscript{45}Al\textsubscript{5} MG). Each atom and its nearest neighbors define a SRO unit. Each SRO unit was radially contracted until the average bond length between the center atom and all neighboring atoms was equal to 1.0.
PPM was performed on each pair of SRO units with the same CN. The PPM alignment process of two SRO units required ~ 200 ms on modern hardware, but all of the alignments are independent, making the total alignment process embarrassingly parallel. An implementation of PPM that takes advantage of this parallelization is available on GitHub at https://github.com/spatala/ppm3d.

Figure 3.6 | An illustration of the motif extraction method. First, SRO units are extracted from the simulated model. Point-pattern matching aligns all pairs of SRO units and the dissimilarity score, $D$, is calculated. All values of $D$ are combined into a dissimilarity matrix for HDBSCAN, which identifies clusters of similar SRO units. The cluster of SRO units corresponding to motif 10Å2 (see Table 6.1) is shown. The “bunches” of atoms around the atomic sites are averaged to create the motif. One motif is created for every cluster of similar SRO units identified by HDBSCAN.

After alignment, four metrics were used to quantify the dissimilarity of the two structures:

$$L^2 = \frac{1}{n} \sum_{i=0}^{n} \left( A_{ix} - B_{ix} \right)^2 + \left( A_{iy} - B_{iy} \right)^2 + \left( A_{iz} - B_{iz} \right)^2$$

where $A_{ix}$ is the x-coordinate of atom $i$ in the SRO unit $A$, etc., and $n$ is lower of the CN of $A$ or $B$;

$$L^1 = \frac{1}{n} \sum_{i=0}^{n} \left| A_{ix} - B_{ix} \right| + \left| A_{iy} - B_{iy} \right| + \left| A_{iz} - B_{iz} \right| ;$$

$$L^\infty = \max \left( \left| A_{ix} - B_{ix} \right| + \left| A_{iy} - B_{iy} \right| + \left| A_{iz} - B_{iz} \right| \right) ;$$

and
\[ L^\alpha = \frac{1}{m} \sum_{i,j} |\angle(A_i, A_j) - \angle(B_i, B_j)| \]

where the function \( \angle(A_i, A_j) \) calculates the angle between atom \( A_i \) and atom \( A_j \) through the center of the SRO unit, \( m \) is the total number of bonds in \( A \), \( i \) and \( j \) are indices of neighboring atoms in \( A \), \( B_i \) is the atom in \( B \) that corresponds to atom \( A_i \) in \( A \) after alignment, and the summation runs over the indices of all pairs of neighbors in \( A \). \( L^\alpha \) is therefore a measure of the mean angular dissimilarity of \( A \) and \( B \). The distribution of values of each of these metrics were normalized to have a mean and standard deviation of 1.0, then the geometric mean of these four normalized metrics,

\[ D = \sqrt[4]{L_2^{\text{norm}} \cdot L_1^{\text{norm}} \cdot L_{\infty}^{\text{norm}} \cdot L_\alpha^{\text{norm}}} \]

was computed. From the dissimilarity, one could also calculate a similarity metric as defined in [196] from \( S = e^{-D} \).

These four metrics were chosen to quantify various aspects of the differences in atomic structure as well as to illustrate the ability to calculate various structural similarity metrics after alignment by PPM. \( L_1 \) puts less emphasis on outliers (poorly matching atoms) than \( L_2 \), while \( L_{\infty} \) only considers the worst outlier. \( V_A \) provides a measure of angular variation to complement the bond length measures of the \( L_p \) metrics. The geometric mean, \( D \), has more discriminating power than any of the individual metrics.

\( D \) values from the pairs of SRO units with the same CN were used to form separate dissimilarity matrices, one for each CN. HDBSCAN [197,198], a machine learning clustering algorithm, was applied recursively to each dissimilarity matrix until the resulting clusters were primarily classified as one noisy cluster. Two properties of HDBSCAN make it especially well-
suited to cluster SRO units: first, it is a spatial clustering algorithm that clusters data based on the local density of points and can therefore identify clusters with non-spherical shapes in \(d\)-dimensional configuration space. This is advantageous because we have a poor understanding of the shape of the data in \(d\)-dimensional space. Second, HDBSCAN has a well-defined notion of noise and can classify points as outliers. Therefore, SRO units with exceptionally strong disorder will be classified as outliers, and their unusual local environments do not influence the identified clusters. (In the context of MG structure, these outlying SRO units may constitute an interesting way to define the concept of a defect.) In addition, the hierarchical nature of HDBSCAN allows for a recursive implementation that can identify clusters with different local densities while automatically identifying the optimal number of clusters.

The result of the recursive HDBSCAN algorithm is one or more clusters of SRO units with the same CN and similar geometry, as defined by the metric \(D\). Each cluster of SRO units produced in this way was used to create a motif. First, all SRO units in the cluster were aligned into the same orientation by using PPM to align each SRO unit to the one SRO unit that was most geometrically representative of the group (defined as the SRO unit with the lowest mean dissimilarity score calculated over all SRO units in the same cluster). Once the SRO units were in the same orientation, the atom-to-atom mappings provided by PPM [191] determine which atom in each SRO unit corresponds to each of the \(n\) atomic sites, where \(n\) is the CN of the SRO units. These “bunches” of atoms around each atomic site represent the disorder of the structure. By averaging the atomic positions in each “bunch,”” the disorder is averaged out and the underlying structure of a group of similar SRO units is identified.

We call the structure that is produced by averaging the atom positions around each atomic site a motif. Each motif is representative of a subset of the SRO units in the original model. One motif is produced per cluster identified via the recursive HDBSCAN algorithm, and collectively
these motifs form the basis for the SRO structure of the material. We emphasize that these motifs are learned from the model with no input or prior knowledge from the experimenter. In addition, it is worth noting that while this discussion has focused on SRO units in particular, in principle the motif extraction method can be applied to any sized structures. The motif extraction code is available on GitHub at [199].

We now discuss the advantages and disadvantages of the motif extraction when compared to other techniques that identify structure in MGs. Approaches to identify prototypical features of MG structure fall into two categories: structures can be derived from hypothesized properties of atoms and their bonds, or structure analysis approaches can identify structural features from simulated atomic models. Examples of the former approach include the Frank-Kasper polyhedra [200,201] and Z-clusters [13,192] (see also Chapter 6.2) as well as structures generated by the ECP model. These structures have in common various ways of defining and enforcing efficient packing and maximizing atomic number density. However, these approaches often lack chemical information beyond that of the shape or atoms (e.g. spherical) and their bond lengths. In addition, the structures that are created are based on known information about MG structure and therefore require significant understanding (or assumptions) of the material structure \textit{a priori}.

On the other hand, in the latter approach, the structural information contained in simulated models is difficult to interpret due to disorder. In the past, motifs have been identified from simulated models by hand by looking at hundreds of SRO units [102,113,202,203], potentially aided by topological characterization techniques such as Voronoi analysis. Unfortunately, this approach is time consuming and is limited by human intuition, which makes it difficult to ensure that all the relevant structures were identified.

Data-driven approaches such as motif extraction offer important alternatives because they remove elements of human limitations. The \textit{cluster alignment} method [195] is similar to our motif
extraction technique in that it is data-driven and removes the disorder from the SRO units in simulated models. In the cluster alignment method, a collective alignment first aligns all SRO units with the same CN with respect to one another simultaneously. Then, the pairwise similarity scores are calculated between all pairs of individual SRO units. The collective alignment results in one compromise structure, which highlights the mean structure of the SRO units but masks the structure variability within a CN, especially for motifs that are representative of a small fraction of the SRO units. In addition, collective, all-at-once alignment means that the similarity scores are compromises with alignment to the collective, rather than one-to-one structural distances between individual pairs of structures. As a result, we expect that density based clustering or other machine learning techniques applied to the dissimilarity matrix generated from cluster alignment would be less successful than what we report here. Our motif extraction method emphasizes structural diversity by calculating accurate pairwise similarity scores using PPM to align individual pairs of SRO units followed by using machine learning clustering to cluster the SRO units into multiple groups with unique structure per CN.

There are drawbacks to motif extraction that may make it unsuitable for certain applications. Motif extraction makes the implicit assumptions that there are a finite number of characteristic motifs that represent the structure and that the model being analyzed contains many SRO units that represent each motif, plus some disorder. The assumption of a small number of motifs will be violated if the disorder in the system is too large, so motif extraction will not be useful for models of a gas and may be not useful for models of colloids at low packing fraction. The assumption of many copies of each motif plus disorder could be violated if the number of atoms in the model is small. Motifs represented by only a few SRO units in a small model may be identified as noise in the HBDSCAN step and therefore not represented by a motif. Neither of these difficulties is present here or in other MG models we have examined in various systems.
including Al-Sm and Pd-Si, in various model sizes ranging from a few thousand to tens of thousands of atoms, and in various model system methods including molecular dynamics and hybrid reverse Monte Carlo modeling [113].

An additional drawback of motif extraction—in contrast to categorization methods such as VI analysis—is that the process of assigning SRO units to motifs is potentially non-unique and thus somewhat arbitrary. Each SRO unit has a dissimilarity score with respect to each motif, and the vector of these dissimilarity scores can be interpreted as a probability of the structure of the SRO unit being “equal to” the structure of each motif. This means that assigning a SRO unit to a single motif oversimplifies the abstraction of the SRO unit’s structure. Put another way, if we make a histogram of all the dissimilarity scores of all SRO units with a given CN aligned to one motif, there is no feature that inspires an obvious cutoff, $D_0$, to assign all SRO units with a dissimilarity less than $D_0$ to the motif. Here, we assigned each SRO unit to the motif to which it is most similar, which provided useful insights.
Medium-Range Structure and Glass Forming Ability in Zr-Cu-Al Metallic Glasses

4.1 An Introduction to Fluctuation Electron Microscopy Structure Studies on Zr-Cu-Al Metallic Glass

Hwang et al. [113] provided a new model for the atomic structure of a Zr\textsubscript{50}Cu\textsubscript{45}Al\textsubscript{5} BMG based on incorporating experimental data on MRO from FEM with an empirical interatomic potential using hybrid reverse Monte Carlo (HRMC) modeling. The models show that the majority of clusters in Zr\textsubscript{50}Cu\textsubscript{45}Al\textsubscript{5} BMG can be classified into two groups: 1) icosahedral-like clusters with approximate five-fold rotational symmetry and 2) crystal-like clusters with approximate four- and six-fold rotational symmetry. Similar VIs group together to form larger superclusters on the MRO length scale. The icosahedral-like clusters form nanoscale chains, while the crystal-like clusters form blobs which exhibit overall four- and six-fold symmetry. A transformation from crystal-like to icosahedral-like clusters is observed after structural relaxation by annealing below the glass transition temperature, $T_g$ [113].

In this chapter [146], FEM experiments and HRMC simulations are combined to study the SRO and MRO of Zr\textsubscript{50}Cu\textsubscript{35}Al\textsubscript{15}, a poorer glass former than Zr\textsubscript{50}Cu\textsubscript{45}Al\textsubscript{5} [204]. The new alloy exhibits the same two icosahedral-like and crystal-like structure types, but differs in its details and thermal stability. Correlations are identified between the nanoscale structure and structural stability in the glassy state with GFA and suggest that efforts to improve GFA should include consideration of destabilizing crystal-like structures as well as enhancing icosahedral structures.

4.2 Experimental and Computational Methods

4.2.1 Samples and sample preparation of Zr\textsubscript{50}Cu\textsubscript{35}Al\textsubscript{15}

The Zr\textsubscript{50}Cu\textsubscript{35}Al\textsubscript{15} samples were prepared by M. F. Besser and M. J. Kramer at the Ames Lab in Ames, Iowa. A mixture of the component elements of 99.9 at.% purity or higher was arc-melted in a Ti-gettered, high-purity argon atmosphere to make a master ingot. The ingot was then
remelted and injected onto a copper wheel spinning at 25 m/sec tangential wheel speed, forming ribbons with ~400 μm thick and 0.5 cm wide. Samples were annealed at 0.83 T_g for 10 min and 60 min to measure the MRO after structural relaxation.

T_g and T_x for the as-cast alloy were measured by P. Zhang using a TA Instruments Q100 Modulated Differential Scanning Calorimeter (DSC) with an autosampler at a heating rate of 0.33 K/s under a flow of purified argon. Annealing for structural relaxation was done in the DSC with an argon environment at 300 ºC (0.83 T_g) for 10 min and 60 min. For annealed samples, we performed a pre-annealing at 200 ºC for 1 min to ensure thermal stability.

Zr_{50}Cu_{35}Al_{15} TEM samples were prepared by P. Zhang by electropolishing. The electrolyte was composed of HNO_3 (9%) with butyl cellosolve + methanol mixture (1:2). The temperature range during the electropolishing was between -42 ºC and -52 ºC. Samples were electro-polished at 42 V using a Struers Tenupol electropolisher [205,206] with a current between 60 and 75 mA. Electropolishing forms a thick oxidation layer on the surface of the sample, so after electropolishing we employed low energy ion milling (Fischione 1040 Nanomill) to remove the oxidation layer. On both sides of the TEM sample, a 60 μm x 25 μm box was milled at -168 ºC with 700 eV for 20 minutes. Immediately before FEM measurements, TEM samples were plasma cleaned at 20 psi Ar + O_2 mixture for ~30 s.

4.2.2 Fluctuation Electron Microscopy Measurements of Zr_{50}Cu_{35}Al_{15}

FEM experiments were performed by P. Zhang at UW Madison in an FEI Titan STEM with a probe C_4 aberration corrector at 200 kV. The Schottky emission gun was operated at 4500 V extraction voltage. Microprobe mode (μP-mode) of the FEI control software with the extended Q range was chosen and a camera length of 512 mm in energy filtered STEM (EF-STEM) mode with a 10 eV wide slit was used. A Gatan annular dark-field detector mounted on the 2.5 mm GIF entrance aperture was used to collect STEM images simultaneously with the nanodiffraction
patterns. The diffraction lens current was adjusted using the FEI free-lens control interface to ensure good diffraction focus. 512x512 pixel nanodiffraction patterns were acquired with a CCD binning of four on a 10x10 grid of positions covering a 30x30 nm² area of the sample. Variance data from ten different areas of each sample were averaged together and reported with one standard deviation of the mean error bars. The exposure time was set to 6 s in order to ensure a sufficiently high signal to noise ratio. The sample thickness was measured using the log-ratio method applied to the elastic scattering transmittance. We used the same elastic mean free path as was used in the Zr₅₀Cu₄₅Al₅ BMG, ~39±1 nm [207]. Typically, the samples had an electron transmittance of 40% ~ 50%, which is thin enough for FEM experiments [206].

Despite the precautions described above, a surface oxidation layer covered the sample even after low energy ion milling. Figure 4.1(a) shows $V(k)$ for the as-cast BMG sample acquired from both the thin and thick regions of the sample. The thinnest region exhibits only one peak at 0.33 Å⁻¹, lower in $k$, which corresponds reasonably well to the lowest order reflections from Zr and Cu oxides, so we assign them to the surface oxide. The thicker region exhibits peaks at 0.33 Å⁻¹ arising from metal-oxygen-metal bonding and peaks at 0.41 Å⁻¹ and 0.45 Å⁻¹ arising from metal-metal bonds, and thus the BMG. The elastic transmittance shows that the oxide-only region is ~20 nm thick and the thicker region is ~50 nm thick, so there is ~30 nm of residual metal. If plural elastic scattering is small, to a good approximation, $V(k)$ from the oxide and the metal simply add. We therefore obtain the signal from just the metal by measuring the signal from just the oxide, then subtracting it from the combined metal/oxide signal, as shown in Figure 4.1(b). Similar measurements of thin, fully oxidized regions, and thicker, partially oxidized regions, are applied to the $V(k)$ data for samples annealed for 10 min and 60 min.
Figure 4.1 | a) \( V(k) \) from thick area and thin oxidation layer of as-cast Zr\textsubscript{50}Cu\textsubscript{35}Al\textsubscript{15} BMG. b) \( V(k) \) after subtracting off the contribution of the oxidation layer. Figure drawn from Ref. [146].

By adjustment of the three full strength condenser lenses, the probe convergence angle \( Q \), and thus the probe size \( R \), can be varied with fixed condenser aperture, enabling variable resolution FEM (VRFEM). VRFEM is the study of \( V(Q) \) at fixed \( k \). That data can be analyzed in the context of the pair persistence model [152] to yield the decay length \( \Lambda \) of an approximate four-body atom position correlation function. \( \Lambda \) is then a measure of the size of the MRO causing diffraction at a particular \( k \). The pair persistence model predicts that \( 1/V \) vs \( 1/Q^2 \) is a straight line, and \( \Lambda \) is derived from the line slope and intercept [152]. We varied the probe size from 1.3 nm to 11.0 nm with nearly constant coherence [208]. The parameters for each probe size are given in Table 4.1. \( V(Q) \) data are not corrected for the surface oxide.

Table 4.1 | The corresponding parameters for five different FEM resolutions. Table drawn from Ref. [146].
<table>
<thead>
<tr>
<th>FEM Resolution (nm)</th>
<th>C2 Aperture (um)</th>
<th>Conv. Angle (mrad)</th>
<th>Spot number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>10</td>
<td>1.17</td>
<td>7</td>
</tr>
<tr>
<td>2.0</td>
<td>10</td>
<td>0.75</td>
<td>7</td>
</tr>
<tr>
<td>5.0</td>
<td>10</td>
<td>0.30</td>
<td>6</td>
</tr>
<tr>
<td>8.0</td>
<td>10</td>
<td>0.20</td>
<td>5</td>
</tr>
<tr>
<td>11.0</td>
<td>5</td>
<td>0.14</td>
<td>4</td>
</tr>
</tbody>
</table>

### 4.2.3 Computational Structure Analysis

Structures for Zr$_{50}$Cu$_{35}$Al$_{15}$ in various states of relaxation were derived from HRMC simulations [111,113,160,161,209]. The HRMC simulations were constrained by SRO from an empirical interatomic potential and MRO from FEM data. The HRMC algorithm uses Metropolis Monte Carlo with random single-atom moves to minimize a cost function $C = \alpha \chi^2 + E$, where $E$ is the system potential energy, and $\chi^2$ measures the discrepancy between the simulated variance $V_s(k)$ and the experimental variance $V(k)$. $\chi^2$ is defined by

$$\chi^2 = \sum_i \left[ \frac{V(k_i) - \beta \cdot V_s(k_i)}{\sigma_{err}} \right]^2,$$

in which $\sigma_{err}$ is the experimental error for each $V(k)$ data point and $\alpha$ is a weighting factor set to encourage energy minimization while constraining the fit of the experimental data within reasonable values (based on the experimental error). $\beta = \frac{1}{3} \frac{t_{sim}}{t_{exp}}$ is a scaling factor that corrects for the thickness difference between the sample and the model and for the approximations in the $V(k)$ calculation [113,163].

The interatomic potential for Zr-Cu-Al was developed by Cheng et al. [109], then modified later by H. Sheng [210]. Hwang et al. used the original version of the potential.

MD in the NPT ensemble at zero pressure in LAMMPS was used to determine the equilibrium density of the Zr$_{50}$Cu$_{35}$Al$_{15}$ glass state at room temperature predicted by the potential. A 2.83$^3$ nm$^3$ box was then randomly filled with atoms with the same atom density and the correct composition, and conjugate gradient minimization in LAMMPS was used to find a local minimum.
of the energy of the structure. The resulting dense random packed structure was used as the input model for each HRMC simulation for the three sample states.

Figure 4.2 shows the convergence of the cost function, energy, $\chi^2$, and the decrease of temperature as a function of step number for the 300 °C, 60 min annealed sample. The result is a model that is close in energy to the MD quenched glass and also in excellent agreement with the experimental FEM data. The HRMC simulations were performed against the oxide-subtracted $V(k)$ data sets with $R = 2$ nm only. The experimental sample thickness, $t_{\text{exp}}$, was 27.0 nm and $t_{\text{sim}}$ was 2.83 nm, giving $\beta = 0.0349$. The weighting parameter between $V(k)$ and $V_s(k)$ was $\alpha = 40$ for consistency with [113].

![Figure 4.2](image_url)

Figure 4.2 | a) System energy, b) $\chi^2$, c) cost function, and d) temperature as a function of step number for the 300 °C, 60 min annealed HRMC simulation. Figure drawn from Ref. [146].

The 3DFT technique was applied to the Zr$_{50}$Cu$_{35}$Al$_{15}$ models to identify MRO structures that give rise to particular features in $V(k)$ for further analysis. This method enables specific features in $V(k)$ to be connected to structures in the model. Models were also analyzed using radial
distribution functions calculated using R.I.N.G.S. [211] and VIIs [212]. The VIIs were grouped into three categories: crystal-like, icosahedra-like, and mixed as defined in Table 4.2 following Hwang et al. [113].

Table 4.2 | VIIs of icosahedral-like, crystal-like, and mixed categories. Table drawn from Ref. [146].

<table>
<thead>
<tr>
<th>Icosahedral-like</th>
<th>Crystal-like</th>
<th>Mixed</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0,0,12,*&gt;</td>
<td>&lt;0,4,4,*&gt;</td>
<td>&lt;0,3,6,*&gt;</td>
</tr>
<tr>
<td>&lt;0,2,8,*&gt;</td>
<td>&lt;0,5,2,*&gt;</td>
<td>&lt;0,3,7,2&gt;</td>
</tr>
<tr>
<td>&lt;0,1,10,*&gt;</td>
<td>&lt;0,6,0,8&gt;</td>
<td>&lt;1,2,5,4&gt;</td>
</tr>
<tr>
<td>&lt;1,0,9,3&gt;</td>
<td>&lt;0,6,0,2&gt;</td>
<td></td>
</tr>
</tbody>
</table>

4.3 Experimental results

Figure 4.3 shows heat release from DSC data for the as quenched and annealed samples. The as-quenched sample shows substantial heat release due to structural relaxation below $T_g$. The two annealed samples show substantially less heat release and are thus in a lower enthalpy state before the DSC measurement.

Figure 4.3 | DSC data for as quenched and annealed samples. Figure drawn from Ref. [146].

Figure 4.4 shows $V(k)$ after oxide subtraction for the as-cast and annealed samples for $R = 2$ nm. One main peak exists at $k \sim 0.41$ Å$^{-1}$, with shoulders near $k \sim 0.37$ Å$^{-1}$ and $k \sim 0.45$ Å$^{-1}$. After
structural relaxation, the amplitude of the peak at $\sim 0.37 \text{ Å}^{-1}$ increases substantially. The peak at $k \sim 0.41 \text{ Å}^{-1}$ increases slightly after annealing for 10 min, then decreases after annealing for 60 min but the changes are not consistently outside the experimental uncertainty. The peak at $k \sim 0.45 \text{ Å}^{-1}$ remains nearly constant.

Figure 4.4 | a-c) Simulated $V_s(k)$ for all three sample states with residuals plotted above show excellent agreement with experimental $V_e(k)$. d) $g(r)$ for all sample states. Figure drawn from Ref. [146].

Figure 4.5(a) shows the change in $V(k)$ (without oxide subtraction) with probe size for the as-cast alloy. The magnitude of $V$ for all three peaks gradually decreases as the probe size increases. When the probe diameter becomes relatively large ($R = 8 \text{ nm}$ and $11 \text{ nm}$), $V$ becomes small and the variation with $k$ becomes very small, indicating that nanodiffraction and thus the sample structure is nearly homogeneous at this length scale. Figure 4.5(b) shows the pair persistent model fitting results of $\Lambda$ for the three peaks identified in Figure 4.4. $R = 11 \text{ nm}$ is removed from the fitting for peaks at $k \sim 0.37 \text{ Å}^{-1}$ and $k \sim 0.45 \text{ Å}^{-1}$ because variance from real structural
information at this resolution is very small compared to variance induced by background sources like small thickness variations or other TEM sample imperfections and the oxide signal. The Pearson correlation $R^2$ for $k \sim 0.37 \text{ Å}^{-1}$ fitting changes from 0.989 to 0.897 if resolution of $R = 11$ nm is included.

![Figure 4.5](image)

Figure 4.5 a) VRFEM plots at five resolutions. The peak at $k \sim 0.37 \text{ Å}^{-1}$ arises from the oxidation layer and the other three peaks due to the BMG. b) The fitting of the decay length $\Lambda$ for three BMG peaks in (a) using the pair persistent model. Figure drawn from Ref. [146].

Similar VRFEM experiments and fitting of $\Lambda$ for all three peaks were carried out for samples annealed for 10 min and 60 min, shown in Figure 4.6 and Figure 4.7 respectively. Compared with the VRFEM results of the as-cast sample at different resolutions, the magnitude of the peak at $k \sim 0.37 \text{ Å}^{-1}$ becomes larger and the peaks at $k \sim 0.41 \text{ Å}^{-1}$ and $k \sim 0.45 \text{ Å}^{-1}$ remain nearly unchanged. The fitting results of $\Lambda$ for different samples are summarized in Table 3. After structural relaxation, the decay length increases for the peak at $k \sim 0.37 \text{ Å}^{-1}$, decreases for the peak at $k \sim 0.41 \text{ Å}^{-1}$, and remains unchanged for peak at $k \sim 0.45 \text{ Å}^{-1}$. The evolution of $\Lambda$ indicates that
structural relaxation mainly occurs during heating and/or the early stage of annealing (first 10 min). All the fitting results are shown in Table 4.3.

Figure 4.6 | VRFEM plots at five resolutions for the sample annealed at $0.83T_g$ for 10 min. Figure drawn from Ref. [146].
Table 4.3 | Decay lengths for as-cast and annealed samples. Table drawn from Ref. [146].

<table>
<thead>
<tr>
<th>Decay length</th>
<th>As-cast</th>
<th>Annealed 300 °C, 10 min</th>
<th>Annealed 300 °C 60, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k=0.45\text{Å}^{-1}$</td>
<td>0.59±0.06 nm</td>
<td>0.56±0.06 nm</td>
<td>0.56±0.06 nm</td>
</tr>
<tr>
<td>$k=0.41\text{Å}^{-1}$</td>
<td>0.86±0.06 nm</td>
<td>0.69±0.05 nm</td>
<td>0.71±0.05 nm</td>
</tr>
<tr>
<td>$k=0.37\text{Å}^{-1}$</td>
<td>0.51±0.06 nm</td>
<td>0.67±0.05 nm</td>
<td>0.66±0.02 nm</td>
</tr>
</tbody>
</table>

4.4 Simulation results

Figures 4.4(a-c) show the final simulated variance $V_s(k)$ for the three samples at the end of the HRMC structure refinement, with residuals plotted above. All three simulated data are in excellent agreement with the corresponding $V(k)$, with a maximum residual of 4.7%. Table 4.4 shows the average atomic energies of the final HRMC models compared to the energy of the MD quenched model. The HRMC model energies are consistently larger than the MD model energies.
due to the competition of minimizing the energy vs. minimizing $\chi^2$, but they are all within a few $kT$ at room temperature.

### Table 4.4 | Final energies for all three simulated sample states compared to MD simulation. Table drawn from Ref. [146].

<table>
<thead>
<tr>
<th>Model</th>
<th>eV/atom</th>
<th>eV/atom above MD</th>
<th>kT at RT above MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD</td>
<td>-5.06054</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starting model</td>
<td>-5.006</td>
<td>0.055</td>
<td>2.13</td>
</tr>
<tr>
<td>t1</td>
<td>-4.968</td>
<td>0.093</td>
<td>3.61</td>
</tr>
<tr>
<td>t2</td>
<td>-4.954</td>
<td>0.11</td>
<td>4.16</td>
</tr>
<tr>
<td>t3</td>
<td>-4.955</td>
<td>0.11</td>
<td>4.12</td>
</tr>
</tbody>
</table>

Figure 4.4(d) shows the total simulated x-ray radial distribution functions for the three final models. All three are essentially identical, indicating similar SRO structures. Figure 4.8 shows an atomic rendering of a region of the final HRMC model for the 60 min, 300 °C annealed sample. The orientation of the model was selected to emphasize the ordered, high rotational symmetry chapter in the center of the model.
Ten additional HRMC runs for the 60 min, 300 °C annealed sample were conducted using different random number generator seeds but with the same starting structure to illustrate the robustness of the HRMC approach. The resulting structures are not identical, but they are qualitatively and statistically similar. All ten have the same disordered and planar regions, and, as shown in Figure 4.9, the VI results for the ten models are statistically similar within the expected $\sqrt{n}$ variability expected for counting (Poisson) statistics. These results indicate that while there are many unique atom configurations that agree equally well with the FEM experimental data, the key features of mixed crystal-like / icosahedral-like regions are common to all of them.

**4.5 Discussion**

Figure 4.10(a) shows that the fraction of crystal-like VI increases with annealing while the number of icosahedral-like VI decreases. This indicates that the planar structure in Zr$_{50}$Cu$_{35}$Al$_{15}$ becomes more crystal-like with annealing at the cost of icosahedral-like local structures. This is also in contrast to the Zr$_{50}$Cu$_{45}$Al$_{5}$ glass in which the number of icosahedral-like VI increases with annealing and the number of crystal-like VI decreases, suggesting that the crystal-like clusters are
more stable and the icosahedral-like clusters are less stable in the poorer glass former than the better glass former. In addition, while the fractions of VI types in both compositions are broadly similar, the Zr\textsubscript{50}Cu\textsubscript{35}Al\textsubscript{15} models have more crystal-like clusters overall than Zr\textsubscript{50}Cu\textsubscript{45}Al\textsubscript{5}, as well as a mean coordination number with one less one atom (11.8 vs. 12.8). The change in mean coordination number implies an overall shift in the local topology of the glasses, which is consistent with the change in composition. In MD simulations of similar MGs [109,213], the fraction of icosahedral-like VI indexes is approximately twice that found for HRMC generated models.

Figure 4.10 | (a) Histograms of the VI categories for the HRMC models. From top to bottom within each bar: Al-centered (green), Cu-centered (orange), Zr-centered (gray) VIIs. (b) Histogram of VI for the most common indices in the model. Bottom axis is sorted by VI type. Figure drawn from Ref. [146].
Despite the increasing number of crystal-like VI with annealing, the size of the crystal-like region in the HRMC models does not change significantly. This indicates that the crystal-like region instead becomes more ordered during annealing. Due to the relatively small size of our simulation models, it is likely not possible for the crystal-like region to grow to larger sizes while correctly reproducing the experimental data and retaining a reasonable energy.

At first glance, the VRFEM results in Table 4.3 seem to tell a different story. The results show that the crystal-like regions shrink while the icosahedral-like regions grow with annealing. This apparent conflict with the simulation results is resolved in two ways. First, it is likely that our HRMC models are too small to accurately model the size of the crystal-like clusters; each model contains precisely one crystal-like cluster near the center of the supercell, so we suspect that the size is constrained by the periodic boundary conditions. Unfortunately, the FEM calculation requires the model size to be an integer multiple of the probe size, and refining a 4×4×4 nm model is beyond our current computational capabilities.

Second, and more interesting, VRFEM and the VI statistics measure different aspects of the structure. VRFEM is primarily sensitive to the size of ordered regions, whereas the VI statistics are also sensitive to the degree or perfection of the structural order. Annealing could therefore make the crystal-like cluster smaller by converting atoms near the surface of the planar structure to icosahedral-like, mixed, or uncategorized and simultaneously make it more crystal-like by converting atoms on the interior from mixed or icosahedral-like to crystal-like. The VRFEM size decreases at the same time the fraction of crystal-like VI increases. This interpretation is consistent with the increase in crystal-like VI and decrease in mixed VI in Figure 4.10 and the lack of change in the Λ associated with the mixed-character peak at 0.45 Å⁻¹.

Figure 4.11 illustrates the 3D FT analysis for the 60 min, 300 °C annealed sample. Figure 4.11(a) and (b) are isosurface images of the 3D FT, which identify volumes in reciprocal space
where significant diffraction occurs. Figure 4.11(c) shows the most important atoms that contribute to the diffraction of the spot-pair circled in Figures 4.11(a) and (b), identified using the filtering, back transform, and smoothing method discussed above. This “sub-model” consists primarily of an ordered cluster of approximately 300 atoms near the center of the supercell, previously identified by hand in Figure 4.8, along with some surrounding atoms. Each of the three pairs of the most intense diffraction spots in Figures 4.11(a) and (b) result in a sub-model consisting of mostly the same atoms. This indicates that each spot-pair results from a different orientation of the same crystal-like structure, which has approximate 6-fold rotational symmetry.

Figure 4.11 | a-b) Two orientations of an isosurface plot of the spots in reciprocal space for the 60 min, 300 °C annealed sample. c) The sub-model that results from the spot-pair circled in (a) and (b). d) The sub-model in (c) reoriented corresponding to the g direction to show the planes of atoms (vertical) that give rise to Bragg diffraction. Figure drawn from Ref. [146].
The vector $\mathbf{g}$ from the center of the 3D FT to each spot is perpendicular to the real space planes that cause the diffraction. By rotating the sub-model in Figure 4.11(c) according to the orientation of $\mathbf{g}$, we can identify exactly which set of planes gives rise to a specific pair of spots. This planar structure is shown (with planes vertical) in Figure 4.11(d). We can connect spots to peaks in $V(k)$ by comparing the length of various $\mathbf{g}$’s to peak positions in $k$. Figure 4.12 shows the normalized intensity as a function of length $|\mathbf{g}|$ for all the spots identified in the computed reciprocal space superimposed on $V(k)$ for the as-quenched sample. The vertical axis is the integrated intensity inside each 3D spot, divided by the average intensity of a shell with the same radius $|\mathbf{g}|$. (The 3D FT is not calculated with experimental convergence, collection angles, or electron scattering factors, so the raw spot intensities are not physically meaningful.) The high intensity spots are clustered around the main peak in $V(k)$ and its shoulders, and there is one strong peak associated with the high $k$ peak centered at 0.7 Å$^{-1}$. The strong correspondence between the spot positions and $V(k)$ peaks emphasizes the origin of the planar structures in the model as arising from the HRMC algorithm forcing the model to match the FEM data.

Figure 4.12 | The length of each $\mathbf{g}$ identified in the computed reciprocal space with respect to $V_e(k)$ for the as-quenched sample. Figure drawn from Ref. [146].

The character of the VI in the sub-models for each $|\mathbf{g}|$, connected by Figure 4.11 to features in $V(k)$, enable peaks in $V(k)$ to be assigned to generalized structural features in the models. As diagnostics, we use $f_{\text{ico}}, f_{\text{xtal}}$, and $f = f_{\text{ico}}/f_{\text{xtal}}$. $f_{\text{ico}}$ is the ratio of the number of icosahedral-like
atoms in a particular sub-model to the number of icosahedral-like atoms in the full model, so it represents the fraction of the icosahedral-like atoms in the full model captured by the sub-model. $f_{xtal}$ is analogous for crystal-like atoms, and $f$ gives a measure of the relative icosahedral-like or crystal-like character of the sub-model. Figure 4.13 shows $f$ as a function of $|g|$ for all three sample states. The data are quite scattered, but there is a trend from more icosahedral- to more crystal-like with increasing $k$. The trend grows more pronounced with annealing, and is strongest for the low and high $k$ shoulders on the main peak in $V(k)$. We therefore identify the right-hand shoulder near 0.45 Å⁻¹ as arising from the more crystal-like structure, and the left-hand shoulder near 0.37 Å⁻¹ as more icosahedral-like. The main peak near 0.41 Å⁻¹ is less clearly defined, but it becomes more crystal-like with annealing and so we identify it as primarily crystal-like. The assignments of the low $k$ shoulder and main peak are the same as what Hwang et al. found by hand for Zr₅₀Cu₄₅Al₅ [113], but now backed by quantitative analysis. Hwang et al. did not consider the high-$k$ shoulder.

Figure 4.13 | Fits to $f = f_{ico}/f_{xtal}$. Solid lines are fits to the data points. Figure drawn from Ref. [146].

Figure 4.14 compares $V(k)$ for the Zr₅₀Cu₃₅Al₁₅ and Zr₅₀Cu₄₅Al₅ BMGs [113] after 300 °C, 60 min annealing. Although the peak positions are not in exactly the same position, likely due to different mean interatomic distances arising from the difference in composition, Zr₅₀Cu₄₅Al₅ shows the same low-$k$ shoulder, main peak, high-$k$ shoulder pattern as Zr₅₀Cu₃₅Al₁₅. The high-$k$
shoulder in particular is much lower in Zr_{50}Cu_{45}Al_{5} than Zr_{50}Cu_{35}Al_{15} and the low-\(k\) shoulder is much higher. The main peak is similar in magnitude. Given the structure assignments for the shoulders above, Figure 4.14 shows that after structural relaxation, Zr_{50}Cu_{45}Al_{5} has stronger icosahedral-like character and weaker crystal-like character than Zr_{50}Cu_{35}Al_{15}.

Figure 4.14 | Zr_{50}Cu_{35}Al_{15} and Zr_{50}Cu_{45}Al_{5} \(V(k)\) for the 300 °C, 60 min annealed sample. Figure drawn from Ref. [146].

The structural evolution on annealing is different for the two samples as well. Although both compositions have a maximum fraction of mixed VI after annealing for 10 minutes, Zr_{50}Cu_{45}Al_{5} becomes more icosahedral and less crystal-like with increasing structural relaxation whereas Zr_{50}Cu_{35}Al_{15} becomes less icosahedral and more crystal-like. In the final state, the crystal-like fraction of VI in Zr_{50}Cu_{35}Al_{15} is higher than in Zr_{50}Cu_{45}Al_{5}, while the icosahedral-like fractions are similar. Taken together, these results suggest that the crystal-like clusters are more thermally stable in Zr_{50}Cu_{35}Al_{15} than in Zr_{50}Cu_{45}Al_{5}, while the icosahedral clusters are either similar in stability or slightly more stable in Zr_{50}Cu_{45}Al_{5}. Higher thermal stability for crystal-like clusters also supports the hypothesis that the crystal-like clusters become more strongly ordered in structure even as they shrink with annealing.

One possible origin for crystal-like order is the fluctuations of embryos leading up to nucleation in the cooling liquid. In that case, stronger crystal-like order may indicate that the cooling liquid came closer to nucleation and crystallization. Similarly, crystal-like order that is
more stable against thermal annealing in the glassy state may indicate lower relative free energy of the crystal-like structure with respect to the icosahedral-like structure, although it could also result from lower atomic mobility.

These results suggest an important role for destabilizing crystal-like structures and enhancing glass formation. Most structurally-based concepts for increasing GFA focus on increasing the stability of the glass structure by efficient short-range packing [130,214,215] or by increasing icosahedral order inconsistent with translational symmetry [133,216]. Our results suggest that the primary difference between Zr$_{50}$Cu$_{45}$Al$_{5}$, a good glass former, and Zr$_{50}$Cu$_{35}$Al$_{15}$, a less good glass former, is better stability of crystal-like structures in the poor glass former. A lower free energy crystal-like state will favor nucleation and growth of the crystal phase, preventing glass formation. GFA criteria based on thermal characteristics like \( T_x \) or \( T_m \) or on phase diagrams like searching for deep eutectics or low liquidus regions (e.g.) implicitly include low stability of the competing crystalline phases. Our results emphasize the structural results of limiting crystal stability and demonstrate an approach to characterizing this contribution to glass stability in amorphous samples, without complete crystallization.

4.6 Summary

A combination of FEM experimental data, HRMC structure refinements, and analysis of the resulting models shows that in the Zr-Cu-Al alloy system, a poorer glass former, Zr$_{50}$Cu$_{35}$Al$_{15}$ has more pronounced and more thermally stable crystal-like medium-range order than a better glass former, Zr$_{50}$Cu$_{45}$Al$_{5}$. Peaks in the experimental FEM data are connected to structure type, crystal-like or icosahedral, based on examining the structure of sub-models of HRMC-derived structures created by locating highly diffracting, planar structures via the three-dimensional Fourier transform of the model. With increasing structural relaxation due to thermal annealing below \( T_g \), the Zr$_{50}$Cu$_{35}$Al$_{15}$ alloy exhibits stronger crystal-like order and weaker icosahedral-like
order, the opposite of the behavior for Zr$_{50}$Cu$_{45}$Al$_{5}$. However, variable-resolution FEM data shows that the length scale associated with crystal-like order decreases with annealing, so the crystal-like regions may be simultaneously shrinking and growing more strongly internally ordered.

The connection between crystal-like medium-range order and glass forming ability suggests that destabilizing crystal-like structure is important to improving the glass forming ability of BMGs in this system. We speculate that the crystal-like order could arise from the fluctuations leading up to nucleation.
5 A Topological Structure Study of Pd$_{82}$Si$_{18}$ HRMC Glasses

The metal-metalloid system Pd-Si forms MGs at high concentration of Pd [ref]. These glasses have a higher concentration of covalent bonding than metal-metal systems such as Zr-Cu-Al as well as different atomic radii ratios. These different chemical properties make the Pd-Si system an interesting follow-up study after studying the Zr-Cu-Al system. Three Pd$_{82}$Si$_{18}$ samples were studied using FEM, HRMC, and VI analyses. The three samples are differentiated by their annealing conditions: as-quenched, annealed at 320 °C for 10 min, and annealed at 360 °C for 1 min.

Figure 5.1 shows the experimental $V(k)$ data for the three glassed collected by FEM experiments performed by P. Zhang. $V(k)$ for the as-quenched sample shows the least variance, and the variance increases with increasing annealing temperature. Peaks appear at 3.8, 4.1, 4.6, and 5.0 nm$^{-1}$ for the 320 °C and 360 °C annealed samples. The differences in $V(k)$ show that the MRO of the three samples are not the same. HRMC simulations were performed similar to those for Zr$_{50}$Cu$_{35}$Al$_{15}$ to generate simulated structures that are consistent with the $V(k)$ data (see Figure 5.1). Ten models were created for each of the three glasses in order to improve the statistics of the VI analysis. Figure 5.2 shows an example model produced by HRMC for the 360 °C glass. An ordered region in the center of the model shows crystallinity analogous to that found in the Zr-Cu-Al glasses studied in Chapter 4 and Ref. [113]. This shows that the Pd-Si system has competing glassy and crystalline MRO structure types, as previously shown for metal-metal glasses [113,146], and suggests that this is a wide-spread phenomenon in MGs.
Figure 5.1 | Experimental and simulated $V(k)$ results for Pd$_{82}$Si$_{18}$ under three different annealing conditions.

Figure 5.2 | An example model produced by HRMC of the Pd$_{82}$Si$_{18}$ glass annealed at 360 °C for 1 min. The silver atoms are Pd and the blue atoms are Si.

Figure 5.3 shows the VI categories of the atoms in the three glasses after categorization according to Table 4.2. The lack of significant differences in fraction shows that Voronoi categorization is unable to capture the changes in structure that are identified via FEM—most notably the split in the $V(k)$ peak near $k = 4.3$ nm$^{-1}$. The spatial distribution of clusters with the same VI provides insight into the structure of the ordered and disordered regions of the HRMC models. Surprisingly, clusters with canonical crystal-like VIs such as $<0 5 2 6>$ and $<0 4 4 4>$ do
not have a high tendency to lie in the ordered region of the HRMC models. Rather, clusters with \( \text{VI} <0\ 2\ 8\ 3> \) fall closest to the ordered region in the HRMC models, but the spatial distribution is not visibly concentrated in the ordered regions (see Figure 5.4), which lie near the center of the models. 3DFT analyses (now shown) identified the crystal-like symmetries in the \( \text{Pd}_{82}\text{Si}_{18} \) models and revealed four- and six-fold symmetry indicative of an fcc lattice, analogous to that in the Zr-Cu-Al system. No quantitative information about the structural changes with annealing was available from the 3DFT data.

Figure 5.3 | The fraction of icosahedral-like, crystal-like, and mixed SRO units in the three different \( \text{Pd}_{82}\text{Si}_{18} \) models generated using HRMC simulations.
Figure 5.4 | The atoms with VI $<0 \, 2 \, 8 \, 3>$, shown in red, are the closest to the ordered regions in the most-annealed Pd$_{82}$Si$_{18}$ HRMC models. However, many $<0 \, 2 \, 8 \, 3>$ atoms fall outside the ordered regions as well, and the spatial distribution is quite homogeneous.

Neither the VI categorization nor the 3DFT results were able to identify meaningful differences in the structure of the three Pd$_{82}$Si$_{18}$ MGs. New structure analysis techniques are required to identify the changes in structure of Pd$_{82}$Si$_{18}$ as a function of annealing as well as the similarities and differences between Zr-Cu-Al and Pd-Si HRMC models. Subsequent chapters apply motif extraction, introduced in Chapter 3.6, to Zr$_{50}$Cu$_{45}$Al$_{5}$ and Pd$_{82}$Si$_{18}$ glasses.
6 Structure Analysis of Zr-Cu-Al MGs using Point-Pattern Matching and Motif Extraction

The VI representation of MG structure has significant explanatory power in metal-metal MGs. Atoms with icosahedral topology such as <0 0 12 0> were shown to correlate with properties including glass-forming ability [102,133,217,218], dynamic heterogeneities [121,219], atomic mobility [133,220], and deformation behavior [221,222]. In particular, in Cu-Zr based MGs [13], icosahedral clusters are slow-moving [133,220] and the fraction of icosahedral clusters increases dramatically as the supercooled liquid approaches the glass transition [102,133,217,218]. It is hypothesized that the glass transition is related to this dramatic increase in the fraction of slow-moving clusters. An increase in the population of slow-moving clusters results in the propagation of rigidity through the liquid and, at a critical threshold, causes the substantial increase in viscosity that defines the glass transition [138,223–226].

In this chapter [191,192], we use motif extraction to reproduce many of the results found by VI analysis in metal-metal glasses by studying two typical MGs, a Zr$_{50}$Cu$_{45}$Al$_{5}$ model quenched via MD and a Zr$_{50}$Cu$_{35}$Al$_{15}$ model generated using HRMC. Application of a new method to a well-studied problem contextualizes the method and sets up future studies for comparison. In brief, the important SRO structure motifs of Zr$_{50}$Cu$_{45}$Al$_{5}$ are identified, including an icosahedral motif and motifs similar to hypothesized idealized clusters. An fcc-like motif is identified in the Zr$_{50}$Cu$_{35}$Al$_{15}$ HRMC glass, confirming that the ordered region has strong fcc-like character.

6.1 Point-Pattern Matching Reveals Geometric Icosahedra in Zr$_{50}$Cu$_{45}$Al$_{5}$

Characterization of SRO clusters in MGs is performed most often using VIs. For example, in Zr-Cu based glasses, the atoms with icosahedral SRO are identified as those with VIs <0 0 12 0>. However, the clusters will not have a perfect icosahedral geometry due to the inherent disorder in the glass. Previous studies classified some VIs with a high number of pentagonal faces and
geometry intuitively related to an icosahedron as quasi-icosahedral [102]. However, while the quasi-icosahedral Voronoi polyhedra resemble an icosahedron, a quantitative basis for this consideration is lacking due to the topological nature of the Voronoi method. Here, we employ the PPM algorithm to analyze the atomic structure of a Zr$_{50}$Cu$_{45}$Al$_{5}$ model glass to address the questions:

1. How distorted are the clusters with VI $<$ 0 0 1 2 0, when compared to a geometrically perfect icosahedron? And

2. How similar are the clusters whose Voronoi polyhedra have a high number of 5-sided faces (some of which are considered quasi-icosahedral) to a perfect icosahedron?

The Zr$_{50}$Cu$_{45}$Al$_{5}$ model used in this work was obtained by quenching a liquid with that composition with 9,826 atoms from 2000 K to 600 K at $5 \times 10^{10}$ K/s using molecular dynamics in LAMMPS using the Sheng embedded atom model potential [109], updated in 2012. After quenching, the glass was equilibrated for 500 ps and the inherent structure was calculated by performing a conjugate gradient minimization of the potential energy. We extracted every cluster from this model using a nearest neighbors a cutoff of 3.6 Å. The VI distribution of these clusters is identical to those of other models produced by the same potential [109]. The coordination number distribution of the clusters is shown in Figure 6.1(a).
Figure 6.1 | (a) The coordination number distribution for the Zr$_{50}$Cu$_{45}$Al$_5$ MG model studied in this chapter. (b) The bimodal distribution (blue) of $D$ for all 2,285 clusters with coordination number 12 in the MG model. The colors show analogous histograms for the sets of clusters with three different VIs, all of which have coordination number 12. Figure adapted from Ref. [191].

Coordination number twelve is the most common, consistent with icosahedral SRO. For each cluster, the bond lengths from the center atom to its nearest neighbors were normalized so their average value was 1.0, then each cluster was compared to a perfect icosahedron using PPM. After alignment, $L^2$, $L^1$, $L^\infty$, and $V_A$ were calculated for each cluster comparing it to the perfect icosahedron. The dissimilarity, $D$, was then calculated using the geometric mean error of the four metrics (see Chapter 3.6 for details).

Figure 6.2 | The mean of the $D$ for clusters with specific VIs with a high number of pentagonal faces. The clusters with VI $<$0 0 12 0$> are well below the cutoff of 0.42, while clusters with VI $<$0 3 6 3$> are well above the cutoff and are therefore do not have icosahedral geometry despite their
high number of pentagonal faces and coordination number of 12. The error bars show one standard deviation of the \( D \) values. The horizontal dotted line designates the \( D \) cutoff of 0.42. Figure adapted from Ref. [191].

We first consider all 2,285 clusters with coordination number 12 after alignment to a target of a perfect icosahedron. Figure 6.1(b) (blue) shows the distribution of the dissimilarities, \( D \), calculated after these alignments. The distribution is bimodal, and the low-\( D \) peak is composed of geometrically icosahedral clusters. Dissimilarity histograms for clusters with VIs \(<0 0 12 0>\), \(<0 2 8 2>\), or \(<0 3 6 3>\) (orange, green, and red, respectively) illustrate the range of \( D \) values associated with clusters with these different topologies.

Figure 6.2 shows the mean and standard deviations of \( D \) for clusters with the most common topologies, categorized by their VIs. Not all of these clusters have coordination number 12, but all the clusters were aligned to a perfect icosahedron, regardless. The clusters with VI \(<0 0 12 0>\) are most geometrically similar to the perfect icosahedron, consistent with the MG literature, as shown by their notably low mean \( D \). The VIs that are most often considered quasi-icosahedral include \(<0 2 8 2>\), \(<0 2 8 1>\), and \(<0 1 10 2>\) [13,194,227–229], and while many of the clusters with these topologies exhibit a low \( D \), they display a wide range of distortions. In addition, the mean \( D \) of clusters with VI \(<0 3 6 3>\) is 0.57. This value is significantly larger than the dip between the two peaks in the total histogram in Figure 6.1(b) at 0.42, so these clusters should not be classified as quasi-icosahedral based on their geometry. Clusters with VI \(<0 0 12 0>\) or \(<0 2 8 2>\) and \( D \) greater than 0.42 tend to be Zr-centered (83% and 62%, respectively). This indicates that Zr-centered clusters with icosahedral topology tend to be more distorted than Cu- or Al-centered clusters with icosahedral topology, consistent with previous findings [109]. The average composition of the nearest-neighbor shells of these same clusters is similar to the overall composition of the model, so there are no compositional abnormalities in the shells of these clusters.
Three clusters illustrate the topological insufficiency of VIs to differentiate the geometry of the structures, while the $D$ provides sufficient descriptive power. A $<0\ 0\ 12\ 0>$ cluster (a) with low $D$ has similar structure to a $<0\ 2\ 8\ 2>$ cluster (b) with low $D$, but different structure than another $<0\ 2\ 8\ 2>$ cluster (c) with high $D$. Figure adapted from Ref. [191].

The distribution of $D$ for $<0\ 2\ 8\ 2>$ topology clusters (green in Figure 6.1(b)) straddles this $0.42$ dividing line between icosahedral and non-icosahedral geometries, despite being widely considered quasi-icosahedral in the MG 310 literature [13,194,227–229]. Figure 6.3 illustrates the geometrical disparity between two $<0\ 2\ 8\ 2>$ clusters. The $<0\ 2\ 8\ 2>$ cluster in Figure 6.3(b) has a low $D$ of $0.25$ and has similar structure to both the perfect icosahedron and the Figure 6.3(a) cluster with $<0\ 0\ 12\ 0>$ topology and $D$ $0.13$. However, the $<0\ 2\ 8\ 2>$ cluster in Figure 6.3(c) has a large $D$ of $0.70$ and is dissimilar in structure to both previous clusters.

These results answer the two questions above. $<0\ 0\ 12\ 0>$ topology is strongly associated with icosahedral geometry, as shown by the histogram in orange in Figure 6.1(b), almost all of which falls in the low-$D$ peak of the total distribution below the $0.42$ cutoff. As illustrated in Figure 6.2, many of the $<0\ 2\ 8\ 1>$ topology clusters are geometrically similar to a perfect icosahedron, as are many clusters with $<0\ 1\ 10\ 2>$ and $<0\ 2\ 8\ 2>$ topologies. However, some clusters with the latter VIs have a $D$ that falls above the geometrically-icosahedral cutoff of $0.42$ and should not be classified as having icosahedral geometry; Figure 6.3(c) shows a specific example. $<0\ 3\ 6\ 3>$ topologies, despite having a fairly large fraction of 5-sided faces and being sometimes considered quasi-icosahedral in the literature [194,229] do not have icosahedral geometry based on their
dissimilarity histogram. In general, PPM alignment and the $D$ score provides a quantitative measure of how icosahedral a cluster is in a way that VIs as a measure of topology do not. PPM and $D$ is a particularly useful discriminator for topologies reported to correspond to distorted, quasi-icosahedral structures.

The question of whether geometry or topology is more important for determining the influence of structure on the properties and processes of MGs remains to be answered. Icosahedral topology is considered important because plastic deformation tends to avoid regions in the structure with a high concentration of icosahedral topology [230]; icosahedral topology regions in the supercooled liquid have slower local dynamics than other topologies [231,232]; and the concentration of icosahedral topology increases significantly as the liquid cools through the glass transition [13,231,232]. However, the energy of clusters depends more on their geometry (bond lengths, bond angles, coordination numbers) than on their topology, so we speculate that the explanatory power of topology arises because it is a proxy for geometry that is robust against disorder and easy to compute. PPM provides a robust, computable method of assessing geometry; future work, such as that in Chapters 6.2, 6.3, and 7, will test its explanatory power for properties and processes in MG systems.

### 6.2 Application of Motif Extraction to a Zr$_{50}$Cu$_{45}$Al$_5$ MD Glass

The motif extraction technique was performed on models at 600 K, 900 K, 1200 K, and 1500 K during the MD simulation after conjugate gradient minimization in order to test whether the motifs change with temperature and to generate a superset of motifs capable of describing the structure at all temperatures. A vast majority of SRO units had CNs ranging from 8-15 in this temperature range. Many motifs at different temperatures were similar—defined via PPM where “similar” motifs had a $D$ value below a certain (temperature dependent) threshold—, so a subset of the total set of motifs at these four temperatures was chosen to represent the SRO structure of
the material at all temperatures. Overall, we identified 30 unique motifs in Zr$_{50}$Cu$_{45}$Al$_5$, shown in Figure 6.4 with orientations chosen to illustrate various symmetry elements in the motifs. We use the notation $n_A$ to label each motif where $n$ is the coordination number of the motif and \{A, B, C, ...\} enumerates the motifs at constant $n$. Motifs with structure most similar to the Z-cluster with the same CN are labeled with an additional superscripted Z.

Every SRO unit in each 50 K snapshot in the MD trajectory was aligned to each motif in Figure 6.4 using PPM, and $D$ was computed for every motif + SRO unit pair. Each SRO unit was assigned to the motif with the lowest $D$ with the same CN as the SRO unit. The number of SRO units assigned to a given motif is henceforth referred to as the population of the motif in the atomic model.
Figure 6.4 | The 30 motifs identified in a Zr$_{50}$Cu$_{45}$Al$_5$ MG arranged by CN. Orientations were chosen to illustrate various symmetry elements, if any exist. Note that it is often difficult to show 2D projections that are representative of the 3D structure. Figure drawn from Ref. [192].
6.2.1 Structure-Property Correlations in Zr$_{50}$Cu$_{45}$Al$_5$

Figure 6.5(a) shows normalized data of the motif population as a function of temperature. In order to highlight the informative changes in these populations, we normalized the motif populations in three ways. First, we divided the population of each motif by the number of SRO units with the same CN as the motif at each temperature. This decouples the change in motif population from the overall change in CN of the material as it is cooled (Figure 6.5(b)). Second, we multiplied by the number of the motifs with the same CN (which varies with CN), which allows for direct comparisons of “populations” of motifs across CNs. That is,

$$P_{\text{rel}}(m, T) = \frac{P(m, T)}{P(n = n_m, T)} * M(n = n_m)$$

where $P(m, T)$ is number of SRO units assigned to motif $m$ at temperature $T$, $P(n, T)$ is the population of clusters with CN $n$ at temperature $T$, $M(n)$ is the number of motifs with CN $n$, and $n_m$ is the CN of motif $m$. Finally, the curves were vertically offset so that the mean value of the normalized populations at high temperature was approximately zero:

$$P_{\text{rel}-0}(m, T) = P_{\text{rel}}(m, T) - \langle P_{\text{rel}}(m, T) \rangle_{T \geq 1700}$$

The result of these normalizations allows for a more robust visual comparison of motifs across temperature and CN and highlights the important changes in the populations of the motifs as the material is cooled.
Figure 6.5 | (a) shows a selection of motifs whose population change noticeably during cooling. The y-axis shows the fraction of SRO units for a given CN that were assigned to a motif after normalization as described in the text. Qualitatively, higher values indicate that more SRO units were assigned to a motif than would be expected if the SRO units were distributed evenly among the motifs with the same CN. (b) shows the change in the fraction of each CN with temperature. In both plots, $T_g$ is marked by a solid vertical line. Figure drawn from Ref. [192].

Figure 6.6 shows the normalized “energy” of each motif. The motifs themselves do not have a well-defined energy, in part because they exist in isolation rather than in the context of a MG environment. To compute the motifs’ energies, first the energy of every atom in the inherent structure of the model from which the motif was learned was calculated from the EAM potential used in the MD simulations, then the mean of the energies for the atoms whose SRO unit was assigned to each motif was calculated. The mean energy of the SRO units changes with CN, so in order to compare the relative energies of motifs across CNs, we subtracted the mean energy of all SRO units with the same CN as the motif from the mean energy of all SRO units assigned to a given motif. This difference in energy is plotted in Figure 6.6, which captures the significantly lower relative energy of motif $12\times^2$ in comparison to all other motifs.
Figure 6.6 | The average energy of SRO units in the 600 K model assigned to each motif after subtracting the average energy of all SRO units with the same CN as the motif. The subtraction allows for direct comparison of the motif energies across CNs. Figure drawn from Ref. [192].

We quantified the chemical order of the 600 K inherent structure by observing the species of atoms at the center and in the shells of the SRO units. Figure 6.7 shows the relative concentration of (a) the center atom specie and (b) the average shell composition with respect to the composition of the model (Zr$_{50}$Cu$_{45}$Al$_{5}$) as a function of CN. Al atoms have a high tendency to both be at the center and be in the shell of SRO units with CN 12. Figure 6.8 shows analogous center-atom and shell composition data for each motif. The numbers in Figure 6.8(a) are divided by those in Figure 6.7(a), and the numbers in Figure 6.8(b) are divided by those in Figure 6.7(b); this allows for a relative comparison of chemistry between motifs with different CNs.
Figure 6.7 | (a) the average center-atom composition of all SRO units in the 600 K model with a given CN, normalized by the composition of the model. (b) the average composition of the atoms in the shell of all SRO units in the 600 K with a given CN, normalized by the composition of the model. Al atoms have an abnormally high tendency to be both at the center and in the shell of SRO units with CN 12. Figure drawn from Ref. [192].

Figure 6.8 | (a) the fraction of Cu-, Al-, and Zr-centered SRO units in the 600 K model assigned to a given motif, normalized to the average composition of all SRO units with the same CN as the motif. Nearly all SRO units with CN 10 are Cu-centered, so the relative center-atom composition of all motifs with CN 10 is 1.0; on the other hand, SRO units with CN 12 can be Cu-, Al-, or Zr-centered so motifs with CN 12 have compositions that differ from the average. (b) the fraction of Cu-, Al-, and Zr- atoms in the shell of each SRO unit assigned to each motif in the 600 K, normalized to the average composition of all SRO units the same CN as the motif. The x-axis ticks are the motifs from Figure 6.4 in alphanumerical order; only the labels for motifs with subscript A are shown for clarity.

6.2.2 Structural Hierarchy of Motifs Similar to Z-clusters in Zr$_{50}$Cu$_{45}$Al$_5$

In their seminal 1958 paper [200], Frank and Kasper described a subset of close-packed, polytetrahedral structures in terms of rings of atoms constrained in a 2D plane. They determined
that for structures with CN above 12, 6-atom rings were favorable over 4-atom rings, and 6-atom and 5-atom rings were the identifying characteristics of close-packed, polytetrahedral structures. Many of the motifs identified in this work benefit from this visual description of planar rings in addition to the quantitative PPM metric. We describe the topology of structures with planar rings using notation analogous to “1-5-5-1”, which would describe a structure with two planar 5-atom rings (usually rotated with respect to each other) and two single atoms on the “top” and “bottom” of the structure (i.e. an icosahedron). Note that this description is subject to the orientation of the 2D projection, but it nevertheless remains useful.

The thirty motifs’ CNs, VIs, and dissimilarities to the Z-cluster with the same CN are shown in Table 6.1. With the exception of CN 8, each CN has a motif with structure similar to the Z-cluster with the same CN. The motif with CN 8 is dissimilar to Z8 likely because SRO units with CN 8 are unfavorable due to their atomic radii and instead form due to fluctuations of atomic nearest neighbors in the liquid. There are nine motifs for CN 12, more than any other CN, which is likely a result of the large chemical diversity of SRO units with CN 12 (see Figures 6.1(a) and 6.7(b)).

Figure 6.10 shows the motif for each CN that is most similar to the Z-cluster with the same CN. The motifs for CN 9-14 follow a clear hierarchy of structure with increasing CN, and the placement of an additional atom in the structure (which increases the CN) is often predictable. The topology of these motifs can be described from lowest to highest CN as 1-4-4, 1-4-4-1, 1-5-4-1, 1-5-5-1, 1-6-5-1, and 1-6-6-1. The single motif with CN 15 (15\(\lambda\)Z) slightly breaks the pattern and has a topology that is 1-6-6-2, possibly because 7-atom rings are unfavorable due to the bond length requirements. Motif 15\(\lambda\)Z is both geometrically and visually similar to Z15, including the two rings of five atoms and the dual-triangular structure between those rings. (These features of the structure are not highlighted in Figure 6.10 and are more easily seen in Figure 6.4 where all
the bonds are visible.) Manual alignment of SRO units with CN 16 in the 600 K inherent structure resulted in a motif with topology 1-6-6-3 and VI <0 1 10 5>. This structure is analogous to motif 15_A^Z where the two teal atoms in Figure 6.10 are replaced by a triangle of 3 atoms and is similar to the Frank-Kasper polyhedron Z16 (D = 0.700). It is noteworthy that the identification of the structure of this CN 16 motif, coupled with PPM, can resolve the topological discrepancy discussed in Chapter 3.3 in Ref. [224] where CN 16 structures transition from VI <0 1 10 5> to <0 0 12 4> as the glass is further equilibrated; rather than relying on the discontinuous change in topology, PPM comparisons to this motif provide an avenue for quantifying a continuous change in structure during cooling.

Table 6.1 | The CN, VI, and dissimilarity score (D) to the Z-cluster with the same CN for all motifs. See Figure 6.9 for context for the dissimilarity scores. Table drawn from Ref. [192].

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<th>Motif Label</th>
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<th>VI</th>
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<td>$&lt;0 \ 0 \ 12 \ 3&gt;$</td>
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Figure 6.9 | A histogram of all dissimilarity scores, $D$, in the 600 K model calculated by motif extraction. Figure drawn from Ref. [192].

6.2.3 Structure and Chemistry of Select Motifs in Zr$_{50}$Cu$_{45}$Al$_5$

Some motifs in Zr$_{50}$Cu$_{45}$Al$_5$ have unique chemical order or correlate with phenomena such as the glass transition; we discuss those motifs in this chapter. SRO units with icosahedral and quasi-icosahedral VI are widely reported to play an important role in the structure and dynamics of Zr-Cu-Al MGs [13,119,233]. Motif $12_A^Z$ is an icosahedral motif with VI $<0 \ 0 \ 12 \ 0>$ and extraordinarily high similarity to the geometrically perfect icosahedron. SRO units most like this motif tend to have an abnormally high number of Al atoms in their shell as well as at the center (Figure 6.8), which is consistent with previous work identifying networks of interpenetrating
icosahedra in Zr-Cu-based MGs [133,223,234,235]. The fraction of atoms assigned to this motif as a function of temperature increases dramatically as the glass goes through its glass transition (Figure 6.5). In addition, motif 12$_{\alpha}^{Z}$'s relative energy is dramatically lower than all other motifs, indicating that this motif is the preferred CN 12 structure. These results are in line with other work [102,115,133,220,236] illustrating the unique properties of icosahedra in Zr-Cu-based MGs and confirm that the motif extraction method identifies structures that correlate with properties.

Motif 12$_{B}$ is the other motif with VI $<$0 0 12 0$, but it is significantly less geometrically icosahedral than motif 12$_{\alpha}^{Z}$. Many SRO units with VI $<$0 2 8 2$ are most similar to this motif, whereas almost all SRO units that are most similar to motif 12$_{\alpha}^{Z}$ have VI $<$0 0 12 0$. We therefore call motif 12$_{B}$ quasi-icosahedral. SRO units assigned to motif 12$_{B}$ tend to be Cu- or Al-centered and their shells are Al-poor relative to the base composition. The fraction of SRO units assigned to this motif increases as the material undergoes the glass transition, but not as dramatically as motif 12$_{\alpha}^{Z}$; however, many more SRO units are most like this motif than motif 12$_{\alpha}^{Z}$, possibly because the structural constraints in the glass prevents these SRO units from being more perfectly icosahedral. Finally, motif 12$_{B}$ has the 2$^{nd}$ lowest energy of motifs with CN 12, again highlighting the stability of (quasi-)icosahedral structures in Zr$_{50}$Cu$_{45}$Al$_{5}$ MGs.

Motif 12$_{E}$ is a CN 12 motif with VI $<$0 2 8 2$. SRO units most similar to it tend to be Zr-centered and their shells tend to be Al-rich. The fraction of SRO units assigned to this motif decreases through the glass transition, despite the fact that it is more stable than the other non-icosahedral motifs with CN 12. This motif represents many of the Zr-centered, 12-coordinated SRO units, and despite the VI $<$0 2 8 2$ sometimes being considered quasi-icosahedral [213,237,238], SRO units with this structure have the opposite trend with temperature as quasi-icosahedral motifs. We therefore do not consider this motif to be quasi-icosahedral. In addition,
motifs 12\textsubscript{E} and 12\textsubscript{B} demonstrate that the topological descriptor of VI $<0\ 2\ 8\ 2>$ can mix together SRO units with distinct structures and properties.

Motif 10\textsubscript{A}\textsuperscript{Z} is the dominant motif with CN 10 and is similar to Z10. It has VI $<0\ 2\ 8\ 0>$ and has bicapped square antiprism geometry. SRO units with CN 10 are nearly all Cu-centered, as is this motif, and it shows no significant chemical ordering in the shell. Most importantly, the fraction of SRO units assigned to this motif increases significantly with temperature, significantly more strongly than the quasi-icosahedral motif 12\textsubscript{B}, but not nearly as strongly as motif 12\textsubscript{A}\textsuperscript{Z}. SRO units with VI $<0\ 2\ 8\ 0>$ have been identified as important in various other studies [102,239–243]. The significant increase in relative population of this motif indicates that it may play an important role in the structure of Zr-Cu-based MGs as well, so this motif may deserve more attention in future studies.

Motif 11\textsubscript{A}\textsuperscript{Z} is a CN 11 motif with VI $<0\ 2\ 8\ 1>$. The fraction of SRO units assigned to this motif increases with temperature and it is the only low-energy CN 11 motif. The other two motifs with CN 11 also have VI $<0\ 2\ 8\ 1>$, demonstrating again that the topological descriptors of VIs can be unable to differentiate between distinct geometric structures.

As a whole, the motifs discussed here provide an abstraction of the structure of Zr\textsubscript{50}Cu\textsubscript{45}Al\textsubscript{5} MG. Because the abstraction is based on geometry, it may be more understandable than the abstractions of SRO provided by analysis techniques such as Voronoi analysis or common neighbor analysis. Amongst the motifs, we find SRO structures that are both stable (Figure 6.6) and whose populations increase during cooling (Figure 6.5). Scoring the SRO units in other glasses with different composition against these motifs using PPM would uncover how SRO changes with e.g. composition or introduction of new elements.
Figure 6.10 | The motif most like the corresponding Z-cluster for each CN, colored to illustrate the planar, ring-like nature of the structures. As the coordination number increases, there is a clear hierarchy of structure and the placement of an additional atom is often predictable. The motifs are colored and bonds are drawn for viewing purposes. Figure drawn from Ref. [192].

6.3 **Comparison to Zr\textsubscript{50}Cu\textsubscript{35}Al\textsubscript{15} HRMC Glasses**

Motif extraction was performed on the Zr\textsubscript{50}Cu\textsubscript{35}Al\textsubscript{15} HRMC glass studied in Chapter 4 in order to compare the structure to that of an MD glass, studied in Chapters 6.1-6.2. While the composition of the MD glass is slightly different (Zr\textsubscript{50}Cu\textsubscript{45}Al\textsubscript{5}), we expect that the local structure motifs are invariant as a function of composition; instead the populations of the motifs likely change with composition [213]. However, the local structure may change due to the different synthesis techniques, as seen by VI analysis (see Chapter 4 and Refs. [109,113]). Indeed, the HRMC and MD glasses have similar motifs, with the exception that the HRMC glass contains motifs with fcc-like symmetry. Figure 6.11 shows a motif with strong fcc symmetry but small angular distortions that make it slightly non-cubic, and the motif has CN 13 rather than CN 12.
Figure 6.11 | The motif identified in the Zr$_{50}$Cu$_{35}$Al$_{15}$ HRMC models that is most similar to crystalline fcc.

Figure 6.12 shows four motifs identified in the Zr$_{50}$Cu$_{35}$Al$_{15}$ HRMC glass with a hierarchy of order. The motif in Figure 6.12(d) is the same motif as in Figure 6.11, shown in a different orientation to highlight the hierarchy of order. The motif in Figure 6.12(c) is an fcc-like motif with CN 12 but the structure is slightly more spherical than the fcc motif shown in Figure 6.11. Careful inspection of Figure 6.12 reveals that the placement of an additional atom to increase the CN of the cluster is predictable. From CN 10 to 11, an atom is placed in the 2-atom ring at the bottom which has fewer atoms close to it in the center 6-atom ring than the 2-atom ring at the top. The placement of this additional atom “flattens out” the 6-atom ring in the center. From CN 11 to 12, the additional atom is placed in the other 2-atom ring—the one at the top—to complete the symmetry; this further flattens out the center 6-atom ring. From CN 12 to 13, an atom is placed in one of the two 3-atom rings at the top or bottom, which are indistinguishable from one another. This completes the hierarchy of ordered motifs found in the Zr$_{50}$Cu$_{35}$Al$_{15}$ HRMC glass. Taken with the hierarchy of motifs identified in the MD model, this shows that the Zr-Cu-Al system may prefer specific SRO structure such as icosahedra and fcc and that SRO structures with different CN take on the characteristics of these structures as much as is geometrically possible.
The clusters most similar to the fcc motifs shown in Figure 6.12(c-d) lie in the ordered region of the HRMC models (see Figure 6.13). In contrast, clusters with geometry similar to an icosahedron lie in the glassy/unordered regions of the models. The ordered, fcc-like region of the HRMC model is the dominant feature of the structure and is what differentiates the structure from MD-generated structures of the same composition. The fcc-like ordered region diffracts incoming waves and produces the high variance in the FEM data, which is a result of the fcc-like motifs in the structure. The fraction of fcc-like clusters is highest in the most-annealed glass, which is consistent with our previous VI and 3DFT analyses. The new result here is the explicit identification of the “crystal-like” motifs with an fcc crystal structure. Previous work [113] had only the suggestion of fcc bonding character from CNA statistics [93]. Motif extraction explicitly identifies structures similar to fcc at a variety of coordination numbers, as shown in Figure 6.12.

Because the motifs identified from the HRMC glasses are similar to the MD glass (with the exception of the fcc-like motifs), we conclude that the main difference between glass structures created using MD and glass structures with more realistic MRO is the existence of fcc-like order. fcc is a close-packed structure and the fact that we find fcc in these glasses, rather than another
crystalline prototype, is consistent with the hypothesis that close-packed local structures are the building blocks of glass structure.

Figure 6.13 | The spatial distribution of the fcc-like motifs with CN 12 (black) and CN 13 (orange) is concentrated in the ordered region of the HRMC models.
Motif Extraction on Pd$_{82}$Si$_{18}$ HRMC and MD Glasses

7.1 Local Structure Controlling the Glass Transition in a Prototype Metal-Metalloid Glass

VI analysis and similar topological methods are less useful for metal-metalloid glasses than for metal-metal glasses. The dominant topology from VI analysis is the tricapped trigonal prisms, but their population does not change significantly with temperature, nor are they reported to exhibit slow dynamics [102,203,244]. So the question remains: Do local structures exist in metal-metalloid glasses that contribute to large increases in viscosity at the glass transition in the same manner that icosahedra do in metal-metal systems?

In order to answer this question [245], motif extraction [192,199] is employed to characterize the structure of a prototype metal-metalloid glass, Pd$_{82}$Si$_{18}$. Motif extraction identifies a bicapped square antiprism (BSAP) structure which has slow dynamics and increases in concentration as the system cools through the glass transition. These results show evidence in simulations for universality of slow, preferred structures playing a central role in the glass transition of MGs and show that geometric structural analysis may succeed where topological analysis does not.

The glass studied was a Pd$_{82}$Si$_{18}$ MG with 9826 atoms quenched using MD in an NPT ensemble from the liquid state at 1800 K to 0 K at 5x10$^{10}$ K/s in LAMMPS [144,210] with an embedded atom potential [244] and a Nose-Hoover thermostat and barostat (at 0 atm). The atomic configurations were extracted at 50 K increments from 1800 K to 0 K and their inherent structures were calculated by conjugate gradient energy minimization in LAMMPS using the same potential. All analyses were performed on the inherent structures except propensity of motion, which was calculated from MD snapshots. Partial structure factors, $S(q)$, were calculated using RINGS [211] and the VI of each atom using Voro++ [246]. The alignment algorithm [191] used by motif
extraction was used to assign each atom to the motif most similar to it. Propensity for motion [231,247] was calculated from the distance each atom moved after 40 ps in an NPT ensemble at 1200 K, averaged over 100 model trajectories initialized with random Maxwell-Boltzmann velocity distributions [231]. For the propensity of motion calculations, the VI of each atom was calculated from the MD snapshot configuration rather than from the inherent structure because the snapshot configuration, and trajectories generated from it, contains the information about the dynamics of the atoms. The dynamics information is lost upon performing the conjugate gradient minimization that produces the inherent structure.

Figure 7.1 shows the internal energy and volume of the system during the MD quench. The simulated $T_g$ is 744 K, estimated from the change in volume of the system. Figure 7.2 shows consistency between the simulated X-ray partial structure factors and previous simulation results on the same system [244]. In the glassy state the nearest neighbor coordination numbers (CNs) range from 8-15 (see Figure 7.3). Si has CN 10 or lower and Pd has CN 11 or higher.

![Figure 7.1](image.png)

Figure 7.1 | Internal energy (black) and volume (red) vs. temperature. The dashed black line shows $T_g = 744$ K. Figure drawn from Ref. [245].
Figure 7.2 | X-ray partial structure factors for the Pd$_{82}$Si$_{18}$ liquid at 1200K agree well with previous results for the same potential [244]. Figure drawn from Ref. [245].

Figure 7.3 | (a) CN distribution at 300 K colorized by atomic specie. Nearly all Si atoms are 9- or 10-coordinated, while Pd atoms tend to be 11-14 coordinated. Figure drawn from Ref. [245].

Figure 7.4(a) and (b) show the evolution of the VI and CN distribution in the models as a function of temperature during cooling. The CN distribution in Figure 7.4(a) changes significantly, especially CN 11, which decreases with cooling through $T_g$, and CN 13, which increases. This behavior is in strong contrast to a typical metal-metal glass, Zr$_{50}$Cu$_{45}$Al$_5$, for which the CN distribution is largely temperature independent (see Figure 7.5). The VI distribution in Figure 7.4(b) has significant temperature dependence, but most of the changes are a result of the changes
in CN, not a result of atomic rearrangements at constant CN (as in metal-metal glasses). Figure 7.4(c) shows the fraction of each VI divided by the fraction of the corresponding CN at each temperature, which normalizes out the effects of the changing CN on the VI distribution. In Figure 7.4(d), the curves are offset so that the high-temperature concentration falls near zero, which highlights the changes in the fraction of CN of each VI. This data captures changes in local topology that are not created by the changing CN distribution. In particular, clusters with VI $<0 2 8 0>$ (CN 10) are more prevalent in the glass than in the liquid, although this change is smaller than the change in icosahedral order in metal-metal glasses [13,102,133,217,218].

Figure 7.4 | (a) The fractions of clusters with different CNs in a Pd$_{82}$Si$_{18}$ MG change significantly with temperature, in contrast to a Zr$_{50}$Cu$_{45}$Al$_{5}$ glass (see Figure 7.5). (b) The fraction of clusters with different VI also change as a function of temperature. (c) Normalizing the fraction of clusters by the fraction of CN shows that changes in CN drive most changes in topology. (d) Replotting the data in (c) with each curve offset to zero at high temperature emphasizes the changes in topology through the glass transition. The fraction of clusters with topology $<0 2 8 0>$ shows a
significant increase during cooling. The fraction per CN of clusters with VI $<0\ 0\ 12\ 0>$ is low. Figure drawn from Ref. [245].

Figure 7.5 | The CN distribution as a function of temperature in a Zr$_{50}$Cu$_{45}$Al$_{5}$ MG, see Ref. [192]. Contrasting this data with the data in Figure 7.4(a), the changes in CN with temperature are much more significant in Pd$_{82}$Si$_{18}$. Figure drawn from Ref. [245].

Neither the change in topology associated with the change in CN nor the change in topology at constant CN identifies the clusters associated with dynamic arrest at $T_g$. Figure 7.6 shows the propensity of motion at 1200 K of the 25 most common VIs in the Pd$_{82}$Si$_{18}$ liquid, sorted from slowest to fastest. The clusters with VI $<0\ 2\ 8\ 0>$, which increase in population, are not particularly slow-moving, unlike icosahedral topologies in metal-metal glasses [133,220]. The other topology that dominates a particular CN, $<0\ 3\ 6\ 0>$ for CN 9, is slower than most of the other topologies, but its concentration changes little during cooling (see Figure 7.4(d)). $<0\ 2\ 8\ 2>$ and $<0\ 1\ 10\ 2>$ topologies have the lowest propensity for motion, but neither one is particularly prevalent, and their fraction of CN changes by less than 5%. In contrast to metal-metal systems, icosahedral topologies are not slow moving, nor do they change significantly in population through $T_g$. Therefore, a structural description using VI analysis does not lead to a clear correlation between structure and the glass transition.
Figure 7.6 | The propensity for motion at 1200 K of the 25 most common VI categories do not reveal an immediate connection between structure and properties. In particular, clusters with VI $<0 \ 2 \ 8 \ 0>$ have intermediate propensity for motion. Figure drawn from Ref. [245].

Figure 7.7 shows the 27 unique motifs identified using motif extraction. We use the notation $n_A$ to label each motif where $n$ is the CN of the motif and $\{A, B, C, \ldots\}$ enumerates the motifs at constant $n$. Table 7.1 lists the motifs, CN, VI, and dissimilarity [191] to the topologically close-packed Z-cluster with the same CN (see Ref. [192] for details). As in a previous analysis of $\text{Zr}_{50}\text{Cu}_{45}\text{Al}_5$ [192], a hierarchy of motifs are identified with increasing coordination number. Some motifs have striking symmetry, such as motif $14A$ and the motifs (denoted with superscript $Z$) are very similar to Frank-Kasper polyhedra or Z-clusters [13]. Some CNs have only one motif, while others have several.
Figure 7.7 | The 27 motifs identified in a Pd$_{82}$Si$_{18}$ MG arranged by CN. Orientations were chosen to illustrate various symmetry elements, if any exist. Figure drawn from Ref. [245].

Table 7.1 | The CN, VI, and dissimilarity ($D$) [191] to the Z-cluster with the same CN for all motifs. For all the pairs of clusters in the model, dissimilarities range from 0.0 to 1.97 with a mean of 1.0 and a standard deviation of 0.16. Table drawn from Ref. [245].

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<td>&lt;0 3 6 0&gt;</td>
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Motif extraction reveals a strong correlation of structure with the glass transition. Out of the 27 unique motifs identified, $10_A^Z$ and $10_B$ are of particular interest (shown in Figure 7.8(a-b)). These motifs have the same VI, $<0\ 2\ 8\ 0>$, and CN 10, but motif extraction decoupled them. The fraction of CN 10 atoms most similar to motif $10_A^Z$ increases dramatically through the glass transition, and the fraction of motif $10_B$ decreases dramatically (see Figure 7.9(a)). These opposing changes largely cancel each other out in the fraction of CN 10 clusters with VI $<0\ 2\ 8\ 0>$. In addition, the propensity for motion of $10_A^Z$ clusters is amongst the lowest in the system (see Figure

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7.9(b)), and the propensity for motion of 10₈ clusters is higher than all but one other structure. The three motifs slower than 10₈, motifs 15₈, 14₈, and 9₈, change very little in concentration through $T_g$. The motif faster than 10₈, motif 8₈, occurs at very low density in the glass.

![Motifs in Pd₈₂Si₁₈ compared to other structures.](image)

**Figure 7.8 | Motifs in Pd₈₂Si₁₈ compared to other structures.** (a) Motif 10₈, (b) motif 10₈, (c) a perfect BSAP, the Z-cluster with CN 10 [13,192], (d) motif 12₈, the most icosahedral motif in Pd₈₂Si₁₈, (e) the most icosahedral motif in Zr₄₅Cu₄₅Al₅ [192] and (f) a perfect icosahedron. 10₈ is similar to the perfect BSAP, but 10₈ is not. 12₈ is significantly less geometrically icosahedral than the extracted motif for Zr₄₅Cu₄₅Al₅ in (e), as illustrated by the square face in the foreground. The BSAP in (c) has a single 4-fold rotation axis shown by the red arrow. One of the 5-fold rotation axes of the icosahedron is shown in (f), but a similar axis exists about every straight line of atoms passing through the center atom.

Motif 10₈ is therefore a slow-moving structure whose population increases as the liquid approaches the glass transition. It is geometrically similar to the BSAP shown in Figure 7.8(c)), which is the most close-packed polytetrahedral structure with CN 10 [192]. The structure can be described as one center atom aligned vertically with an atom on the top and another on the bottom, and two rings of four atoms in horizontal planes above and below the center atom, rotationally offset by 45°. An icosahedron is similar, except that the four-atom rings are replaced with five-atom rings and the rotational offset is 36°. However, unlike an icosahedron, a BSAP has a crystallographically allowed rotational symmetry. A BSAP has four-fold symmetry, but only about one axis, shown in Figure 7.8(c), whereas an icosahedron has six axes of five-fold symmetry.
Although we have focused on BSAP clusters in Pd_{82}Si_{18} here, there are icosahedral clusters in Pd_{82}Si_{18} and BSAP clusters in Zr_{50}Cu_{45}Al_{5} [192]. In Pd_{82}Si_{18}, there is a motif with VI <0 0 12 0>, 12C (Figure 7.8(d)), but geometrically, it is barely icosahedral compared to the <0 0 12 0> motif in Zr_{50}Cu_{45}Al_{5} (Figure 7.8(e)), which has nearly perfect icosahedral geometry. The 12C motif represents 5% (see Figure 7.10) of the glassy model and has intermediate propensity for motion (see Figure 7.9(b)). Given the unfavorable atomic radii and the potential for some influence of covalent bonding [141], the lack of icosahedral structure in Pd_{82}Si_{18} is not surprising. In Zr_{50}Cu_{45}Al_{5}, the population of BSAP clusters increased significantly as the supercooled liquid approached \( T_g \), with only the icosahedral motif increasing more dramatically.
Figure 7.9 | (a) The change in the fraction of CN for the eight motifs whose fraction of CN changes the most during cooling and motif 12C, normalized as in Figure 7.4(d). (b) The propensity for motion at 1200 K of each motif. $10\alpha^Z$ is amongst the slowest motifs, and $10\beta$ is amongst the fastest. In general, close-packed Z clusters tend to have a low propensity for motion. Figure drawn from Ref. [245].

![Graph showing change in fraction of CN and propensity for motion](image)

Figure 7.10 | Data from Figure 7.9(a) without offsetting the curves to 0.0 at high temperatures. This data shows both the dramatic increase in the fraction per CN of motif $10\alpha^Z$ as well as the low fraction per CN of motif 12C. Figure drawn from Ref. [245].

Overall, these results support the hypothesis that there are preferred nearest-neighbor atomic clusters that exist in the liquid state and both grow in concentration and slow in dynamics more quickly than other structures as the liquid is cooled through the glass transition [115,248,249]. This phenomena is reminiscent of the cooperative rearranging regions and growing dynamical length scale of physical theories of the glass transition [44,250], although proving that connection is beyond the time scales accessible to molecular dynamics simulations like ones analyzed here. The nature of that local structure of course depends on the materials system. For metals, our results suggest that a small set of motifs are responsible for the glass transition, with icosahedra dominant in some glasses and BSAPs dominant in others. That said, we cannot rule out that in systems with different bonding characteristics, both icosahedral and BSAP geometries could be unfavorable and a different motif might play the same functional role.
Finally, these results demonstrate the utility of a structural abstraction involving geometry, as opposed to topology, in identifying structure-property correlations. Whether the BSAP structure is connected to other properties like plastic deformation the same way icosahedra are remains to be seen, but the properties of a material are fundamentally controlled by interatomic energies, and these energies are strongly determined by relative atom positions, \textit{i.e.} geometry. Because topological analysis techniques discard information about the relative atom positions, the information contained in topological descriptions of structure is less directly linked to the atomic energies. Therefore, while motif extraction and VI analysis provide complementary information, we believe (and our evidence shows) that motif extraction provides a structural description that is more closely connected to materials’ properties.

In conclusion, we have identified a close-packed, local structure motif, the bicapped square antiprism, in Pd$_{82}$Si$_{18}$, a model metal-metalloid glass-forming alloy, that plays a significant role in the glass transition. This motif is among the slowest moving local structures in the supercooled liquid, and it increases in concentration significantly through the glass transition. This motif was identified using \textit{motif extraction}, a machine learning method for extracting the geometry of characteristic structure from disordered atomic models. The BSAP motif has the same VI (<0 2 8 0>) as another local structure with the opposite behavior, which masks the structure-property relationship from topological measures like VI. These results support the general conclusion that across metallic liquids, preferred nearest-neighbor atom clusters exist which play an outsized role in dynamic arrest during the glass transition.

\section*{7.2 A Geometric Structure Study of Pd$_{82}$Si$_{18}$ HRMC Glasses}

The same three Pd$_{82}$Si$_{18}$ HRMC models studied in Chapter 5 were analyzed using motif extraction in this chapter. The three samples are differentiated by their annealing conditions: as-quenched, annealed at 320 °C for 10 min, and annealed at 360 °C for 1 min. Similar to the work
in Chapters 6 and 7.1, motif extraction was used to identify the statistically significant SRO structure in the Pd$_82$Si$_{18}$ HRMC models. After the motifs were identified, each atom was assigned a VI and a motif based on its local structure. A cutoff of 3.45 Å was used as the nearest neighbor cutoff to generate the clusters.

Unlike topological analyses, motif extraction identifies the local structures that are most prevalent within the order region at the center of the HRMC models. Three fcc-like motifs were identified in the HRMC models, shown in Figure 7.11. The motifs have a similar hierarchy of structure as the CN 11-13 motifs in the Zr$_{50}$Cu$_{35}$Al$_{15}$ glasses. Two motifs with CN 10 were identified but neither have the same structure as the fcc-like motif in the Zr$_{50}$Cu$_{35}$Al$_{15}$ glasses. The change in atom environment from Si to Pd at CN 10 to 11 makes the lack of continuity in the structure of the motifs from CN 10 to 11 unsurprising. Instead, the fcc-like motifs are all Pd-centered, which is consistent with the high concentration of Pd-centered clusters with CN near 12. Figure 7.12(b) shows that clusters similar to the motif that is most strongly fcc (shown in Figure 7.11(b)) have a strong tendency to lie within the ordered regions. The spatial distribution of fcc-like motifs is contrasted to the spatial distribution of clusters with identical VIs that lie closest to the ordered region, $<0 \ 2 \ 8 \ 3>$, shown in Figure 7.12(a); the distribution of clusters described by their topology has much lower spatial heterogeneity than clusters described by their geometry.

There is no Si-centered motif with a strong tendency to lie in the ordered region of the models, nor is there a Pd-centered or Si-centered motif with a strong tendency to lie outside the ordered regions. Instead, the clusters similar to the non-fcc motifs are homogeneously distributed. This difference is likely driven by the difference in atomic size of the two species, reflected by their coordination numbers. Pd atoms have a peak in their coordination number near 12, consistent with fcc ordering, while Si atoms have a peak at 10, which is inconsistent with fcc ordering (see Figure 7.3). There is, however, no statistically significant mean composition difference between
the ordered region of the HRMC models and the surrounding region. The existence of significant 12-fold coordination around Pd atoms may explain also why the ordered region in both Pd$_{82}$Si$_{18}$ and Zr$_{50}$Cu$_{35}$Al$_{15}$ favors an fcc-like structure.

Figure 7.13 shows that the population of the various types of motifs in the Pd$_{82}$Si$_{18}$ models is largely unchanged by structural relaxation by annealing, in contrast to the behavior in Zr$_{50}$Cu$_{35}$Al$_{15}$ (see Chapter 4 or Zr$_{50}$Cu$_{45}$Al$_{5}$ (see Ref. [113]). The motifs were categorized as glassy or crystal-like based on their mean proximity to the ordered region in the HRMC models. In the metal-metal systems, the reduced enthalpy after annealing is correlated to a change in the population of various motifs. Since that is not the case for Pd$_{82}$Si$_{18}$, we speculate that the reduction in enthalpy may be related to a change in the degree of order within each motif. That is, atoms shift by small distances that increase the degree of structural order and decrease the energy but do not swap neighbors or change local coordination environments. Such small shifts could be, for example, viewed as annihilating sub-atomic free volume.

![Figure 7.11](image)

Figure 7.11 | The three fcc-like motifs identified in the Pd$_{82}$Si$_{18}$ HRMC models have a similar hierarchy of order as the fcc-like motifs with CN 11-13 in the Zr$_{50}$Cu$_{35}$Al$_{15}$ glasses.
Figure 7.12 | (a) The atoms with VI \(<0\ 2\ 8\ 3>\) are the closest to the ordered regions in the most-
annealed Pd\(_{82}\)Si\(_{18}\) HRMC models. This data is also shown in Figure 5.4 and duplicated here for
easy comparison to (b). (b) The atoms with local structure most similar to the fcc motif (shown in
Figure 7(b)) are closest of the motifs to the ordered regions in the same models. The atoms
identified by their VI show significantly less spatial heterogeneity than the clusters identified by
their similarity to the fcc motif.

Figure 7.13 | The number of glassy, crystalline, and unknown clusters in the three Pd\(_{82}\)Si\(_{18}\) HRMC
models, where the local structures were quantified by the motifs. Glassy motifs were identified as
those with a tendency to be outside of the ordered regions in the HRMC models, and crystalline
motifs were identified as those with a tendency to be inside the ordered regions.
8 Structure Analysis of Al$_{92}$Sm$_8$ Metallic Glasses Synthesized Using Different Processing Methods

High Al-content glasses are interesting as potentially inexpensive, high strength, high corrosion resistant materials [251]. Al$_{92}$Sm$_8$ is the best glass former in the Al-Sm system and is a marginal glass former in the context of other MG systems. In this work, two Al$_{92}$Sm$_8$ glasses were synthesized by the Perepeko group at UW Madison using the melt-quenching and mechanical deformation (also known as cold-rolling) [252] processes. The two glasses show different crystallization behaviors [253]. The melt-quenched glass undergoes primary fcc-Al crystallization upon heating. The glass synthesized via cold-rolling crystallizes directly to intermetallic phases without the formation of fcc-Al [253]. Previous work using FEM has connected the primary crystallization behavior of the quenched glass to the presence of small crystal-like regions, frozen in during cooling, which provide catalytic nucleation sites for the formation at relatively low temperature of fcc-Al nanocrystals at high density [254]. The cold-rolled glass has different MRO as shown by different peaks in $V(k)$, but the exact structure was not understood.

P. Zhang conducted FEM experiments to measure $V(k)$ and access information about the glasses’ MRO. The $V(k)$ data are shown in Figure 8.1. Data for the quenched glass are consistent with previous measurements, showing a main peak at 0.43 Å$^{-1}$, consistent with the Al <111> reflection and a should at 0.47 Å$^{-1}$, consistent with the Al <200> reflection. There is no peak at 0.7 Å$^{-1}$ which is the location of the <220> reflection [254]. The cold rolled glass shows the same 0.43 and 0.47 Å$^{-1}$ peaks, as well as a higher variance in the $k$ range from 0.36 to 0.43 Å$^{-1}$. This is the same range as the main peak in $V(k)$ from a cold-rolled glass in previous work [254], and it is lower in $k$ than any crystalline Al reflection. There may also be smaller peaks at intermediate $k$ near 0.56 Å$^{-1}$ and 0.62 Å$^{-1}$. Little quantitative information about the structure of the glasses beyond
these qualitative descriptions is available from direct comparison of the $V(k)$ data for the two glasses.

![Figure 8.1](image1.png)

Figure 8.1 | $V(k)$ for the quenched and cold-rolled Al$_{92}$Sm$_8$ glasses.

FEM data provides the critical information to run HRMC simulations to generate atomic structures of the quenched and cold-rolled glasses that are consistent with the experimental data. Figure 8.2 shows an example HRMC model that is consistent with the cold-rolled FEM data. An ordered region of crystal-like clusters exists in the center of the model and a similar region exists in the HRMC models consistent with the quenched glass’s FEM data. The CN distribution for the cold-rolled glass is shown in Figure 8.3. There is no evidence for phase separation of pure Al in these models (see Figure 8.4), consistent with MD simulations on a similar glass [255]. The ordered region in these Al-Sm glasses are also similar to the ordered regions found in HRMC models of Pd$_{82}$Si$_{18}$ and Zr-Cu-Al MGs. For example, all three systems exhibit fcc-like clusters in the ordered region. Ten unique models were generated for both the quenched and cold-rolled glasses to increase the statistics for subsequent analyses. The HRMC models for the two glasses have different simulated FEM signatures, so the atom positions in the models contain information
that differentiates the two glasses. Our structure analysis techniques can quantify those differences, which ideally shed light on the differences in properties (\textit{i.e.} crystallization behavior in this case).

Figure 8.2 | An example HRMC model consistent with the cold-rolled FEM data.

Figure 8.3 | The CN distribution for the cold-rolled Al$_{92}$Sm$_8$ glass.
Figure 8.4 | Sm-Sm partial $g(r)$s for the quenched and cold-rolled samples. Due to low statistics, the $g(r)$ curves are averaged over the ten HRMC models for both the quenched and cold-rolled glasses. The averaged curves are indistinguishable, illustrating that the Sm-Sm bonding and interatomic distances are the same in quenched and cold-rolled glass structures.

Figure 8.5 shows the fractions of the twenty most common VIs in the quenched and cold-rolled glasses. The fractions of $<0\,4\,4\,4>$ and $<0\,5\,2\,6>$ VIs, which are crystalline VIs, are larger in the cold-rolled glass than in the quenched. The fractions of $<0\,3\,6\,4>$ and icosahedral $<0\,0\,12\,0>$ VIs are also larger in the cold-rolled glass. Typically, a higher fraction of icosahedral-like VIs are found in higher stability glasses [13,113,146], and a higher fraction of crystal-like VIs are found in lower stability glasses [112,113,146,194,256]. The data here shows that the fraction of both icosahedral-like and crystal-like VIs are higher in the cold-rolled glass. Unfortunately, these results do not point towards an immediate correlation between structure and crystallization behavior, so we also applied motif extraction to identify the important local structures [36] in the two glasses.
Motif extraction identified motifs in both the quenched and cold-rolled glasses, and we combined those motifs (after removing duplicates) into a superset of motifs to describe the structure of these glasses using the same set of motifs. The cutoff radius used by motif extraction was 3.8 Å for Al-Sm. Three fcc motifs and two partially-fcc motifs were identified, as well as an icosahedral motif. Figure 8.6 shows (a) the fcc motif with CN 12 which is structurally similar to the fcc-like motifs with CNs 11 and 13, (b) the icosahedral motif, (c) an fcc-like motif with CN 12, and (d) a partially fcc (lower) and partially icosahedral (upper) motif with CN 12. The fcc-like motifs with CN 11, 12, and 13 show a hierarchy of structure analogous to the hierarchy seen in both Zr$_{50}$Cu$_{35}$Al$_{15}$ and Pd$_{82}$Si$_{18}$ MGs, and the lone motif with CN 10 has the same structure as the fcc-like motif with CN 10 in Zr$_{50}$Cu$_{35}$Al$_{15}$, shown in Figure 6.12(a). The fcc motifs with CN 12 and 13 are nearly identical and have extraordinarily strong symmetry in comparison to the other motifs identified because they have multiple rotational symmetries and multiple orientations for those rotational symmetries. The fcc motif with CN 11 also has strong symmetry, but the
deviations from the perfect fcc atom positions are higher in this motif than in the fcc motifs with CN 12 and 13. The motif with CN 10 does not have strong fcc-like order because the CN is significantly different, but it follows the same fcc-like hierarchy of order as the fcc-like motifs with CN 11-13.

The spatial distributions of the motifs shown in Figure 8.6 in the ten quenched and cold-rolled models are shown in Figure 8.7. Figure 8.7(a-b) show that clusters most similar to the fcc motifs lie predominantly in the ordered regions (centers) of the HRMC models. Clusters most similar to the icosahedral motif lie outside the ordered regions of the models (Figures 8.7(c-d)). The two partially-fcc motifs have aspects of very local fcc-like symmetry, but do not fully conform to fcc symmetry. The spatial distribution of clusters similar to this motif is homogeneous (Figures 8.7(e-h)).

Figure 8.6 | Four motifs in the Al\textsubscript{92}Sm\textsubscript{8} system: (a) the crystalline fcc motif; (b) the icosahedral motif; (c) a motif with partial-fcc symmetry and a 3-6-3 ring structure; (d) a partially fcc (lower) and partially icosahedral (upper) motif. All of these motifs have CN 12.
Figure 8.7 | Distributions of different motifs in the HRMC models for the quenched (left) and cold-rolled (right) glasses. (a-b) The crystalline-fcc motif shown in Figure 8.6(a) with CN 12 and the nearly identical motif with CN 13; (c-d) The icosahedral motif shown in Figure 8.6(b); (e-f) The motif shown in Figure 8.6(c); (g-h) the motif shown in Figure 8.6(d).
All four of the motifs with fcc symmetry are more commonly found in the cold-rolled glass than in the quenched glass. Figure 8.8 shows the mean dissimilarity, $D$, of the clusters assigned to each motif where $D$ was calculated using PPM by aligning each cluster to the motif to which it was most similar. The mean and standard deviations of the $D$ values give insight into the structural disorder of the relative atom positions for each motif. The results in Figure 8.8 show that the fcc clusters in the cold-rolled glass have less disorder than the fcc-like clusters in the quenched glass. Figure 8.9 shows that the fraction of clusters that have low symmetry is higher in the quenched glass, indicating that its structure has a higher variety of structure types and more disorder than the cold-rolled glass. The number of fcc-like motifs is high in comparison to HRMC models in the Zr-Cu-Al and Pd-Si systems, indicating that Al-fcc units contribute significantly to the structure of these glasses, even in the quenched glasses, despite the lack of long-range crystalline order.
Figure 8.8 | The mean dissimilarity, $D$, of each cluster with respect to the motif to which it is most similar in (a) the cold-rolled glass and (b) the quenched glass. The error bars are the standard deviation of the dissimilarities and therefore represent the spread in the values.
These motif results are consistent with the VI results, and therefore still do not provide an obvious reason for the primary fcc-Al crystallization seen in the quenched glass [253]. Fcc-Al clusters, which we hypothesized catalyze crystallization, are present in both glasses, but they are more strongly present in the cold-rolled glass which does not exhibit primary Al crystallization. We have tested various possible explanations to little avail. For example, composition segregation might create a shell of slow-moving Sm atoms around the fcc-like ordered region in the cold-rolled models, preventing growth into a full fcc crystal. However, no such region exists. There is similarly no evidence for the ordered regions in the cold-rolled glass being fcc in structure but having a different composition for the center atoms of the motifs, preventing the formation of pure-Al nanocrystals. Nor can we find a distinct structural feature associated with diffraction into the broad peak in $V(k)$ at low $k$ in the cold-rolled glass.
This leaves two possible explanations. One is that the greater order in the cold-rolled glass somehow suppresses Al crystallization. Perhaps the hypothesis that the crystallization proceeds directly from the ordered regions is incorrect. Instead, there may be some intermediate stage required, which is incompatible with the greater crystal-like order of the cold-rolled glass. If greater order means greater energetic stability, perhaps the cold-rolled glass structure cannot transform to the required intermediate state for Al crystallization.

The other possibility is that the cold-rolled glass is insufficiently amorphized by deformation. Compared to the previous nearly monolithic cold-rolled glass [254], the samples analyzed here consisted of amorphous regions ~100 nm wide contained within remaining polycrystalline material. The amorphous regions, although they showed only fuzzy rings in electron diffraction, may retain some local, nanoscale crystallinity from the parent crystal foils. In addition, due to the small size of the amorphous regions, we cannot confirm explicitly that these cold-rolled glasses exhibit the same crystallization behavior as the monolithic cold-rolled glass. Upon heating, the crystal regions will grow into the amorphous regions before crystallization with the layers occurs.

Alternatively, the SRO measured here may be insufficient to explain the changes in MRO seen in the FEM data. The VI and motif extraction analysis methods measure the SRO of the materials, while FEM measures MRO. The MRO of a material is inherently dependent on the SRO, but materials can have structures with similar SRO but different MRO based on different packings of the SRO. The VI and motif results for the two Al<sub>92</sub>Sm<sub>8</sub> glasses studied here show that the two glasses have similar, although not identical, SRO. 3DFT analysis (not shown) identified that the peaks in \( V(k) \) arise from the ordered regions in both glasses, including for the \( V(k) \) signal at low \( k \). Unfortunately, the SRO analyses performed here are insufficient to explain the differences in \( V(k) \) of the two glasses.
Finally, the differences in the FEM data indicate that it may be possible for polyamorphism to exist in the Al$_{92}$Sm$_{8}$ glass system. Polyamorphism is the amorphous equivalent of polymorphism and, in the strictest definition, is the existence of two glassy or liquid states with a first-order (discontinuous) phase transition between the two states. However, identifying and inducing the processing condition that facilitates one glass/liquid state to transition into the other, and vice versa, is often an insurmountable task, so proof of polyamorphism in the literature is scarce [257–260]. One sign of polyamorphism is the existence of two glassy states with different densities, as in the case of ice [259,260], SiO$_2$ [58] and Ce$_{55}$Al$_{45}$ [258]. Metallic systems with the potential for $f$-electron delocalization are especially amenable to poly(a)morphism, and the Ce$_{55}$Al$_{45}$ MG is one example. Sm has been shown to have similar $f$-electron behavior as Ce [261], so the Al-Sm system may contain examples of polyamorphism. The differences in the FEM data for the two glasses studied here, which are created using different synthesis methods, lends credence to that idea. However, our HRMC results do not show significant evidence for polyamorphism, and precise density measurements are difficult to perform. The HRMC models presented here are not unique and may be subject to small size effects, and other models with significantly different structure may be consistent with the experimental FEM data. We therefore cannot rule out polyamorphism between these two glassy states, but also cannot confirm the existence of polyamorphism without identifying the glass-to-glass or liquid-to-liquid process that induces a first-order phase transition.
9 Electron Microscopy Characterization of a-Si Films

Amorphous silicon (a-Si) is a prominent material in solar cell technology, although it has recently been largely replaced by other materials, including crystalline silicon (c-Si). Despite significant efforts to grow a-Si films with different structure, all forms of a-Si created using various synthesis methods have indistinguishable structure [151,262–264]. The structure of a-Si is paracrystalline [111,265] with subcritical nanocrystals embedded in an amorphous matrix. The nanocrystals have a diamond-cubic crystal structure and do not grow significantly upon heating, rendering the material XRD-amorphous.

Recently the Hellman lab at University of California, Berkley synthesized a-Si samples using electron-beam evaporation. The samples have abnormally large changes in density, up to 35% higher than standard a-Si and c-Si [266] when grown thin at low temperature and high growth rate (see Figure 9.1). We performed TEM structure studies of the a-Si thin films with the goal to help explain the large changes in density. FEM measurements revealed an anomalous MRO structure signature for films grown above room temperature.

Figure 9.1 | Density of a-Si thin films grown at various temperatures, thicknesses, and growth rates. The dotted black line shows the density of c-Si. Figure was drawn from F. Hellman’s 2018 American Physical Society presentation [266] and the data in this figure was collected and analyzed by the Hellman group.
9.1 Characterization Methods and Method Parameters

Members of the Hellman lab prepared a-Si thin films at 23 °C, 250 °C, 450 °C, and 550 °C with thicknesses of approximately 25 nm (see Figure 9.2). The samples were grown on 50x50 μm, 50 nm thick silicon nitride (SiN) TEM windows at a rate of 0.5 Å/s. We contributed to the film characterization by analyzing the films using HRTEM, electron energy loss spectroscopy (EELS), and FEM methods. The film at 550 °C was crystalline and therefore was not included in most analyses. A small number of nanocrystals were present in the 450 °C film. Nanodiffraction patterns were collected on a FEI Titan at 200 kV in the microprobe STEM mode with probe aberration correction and a camera length of 840 mm. A GIF energy filter with a slit width of 20 eV filtered out the signal of inelastically scattered electrons. A 2 nm coherent beam was formed with a 0.6 mrad convergence angle. One hundred 512x512 pixel nanodiffraction patterns were acquired in a 10x10 grid in a 25x25 nm² area using a Gatan US1000 CCD camera, and the acquisition time for each diffraction pattern was 6 s. EELS spectra were collected on the same FEI Titan instrument in EFSTEM mode with the following parameters: a camera length of 160 mm, a probe convergence angle of 25 mrad, a collection angle of 52 mrad, and an energy dispersion of 0.05 eV/channel. The energy resolution was measured to be 0.8 eV using the full-width at half-maximum of the zero-loss peak. HRTEM images in the planar orientation were taken on a FEI Tecnai-TF30 microscope with a field emission gun source operating at 300 kV. Images with resolution 2048x2048 were collected by a Gatan Ultrascan CCD camera using 1 s exposure time.

EELS measurements were performed on the three a-Si samples and the results were compared to c-Si data in literature [267,268]. EELS measures the energy lost from inelastic scattering from narrow bandwidth electrons due to plasmon interactions. EELS data, therefore, quantifies local electron density and is insensitive to voids in a material. c-Si has an EELS peak at 16.6 eV [267].
Figure 9.2 | A histogram of thickness measurements from FEM nanodiffraction patterns of the 450 °C a-Si film reveals a uniform thickness ranging from approximately 24.4 to 26.1 nm.

9.2 a-Si Results

Figure 9.3 shows a HRTEM focal series for the 23 °C, 250 °C, and 450 °C films. A focal series consists of under-focused, in-focus, and over-focused images on the same region of the sample. Under-focusing and over-focusing accentuates features by increasing the contrast with respect to the in-focus image. HRTEM images of the film grown at 23 °C reveal a columnar structure with low-density regions of size 1-2 nm outlining high-density columns of size 5-15 nm. The HRTEM images of films grown at 250 °C and 450 °C do not show the same columnar structure but, rather, show the canonical features of amorphous films. Careful care was taken to avoid imaging nanocrystals in the 450 °C sample. In addition, there is no evidence for voids in any of the samples. Voids smaller than ~ 5 nm likely cannot be imaged using HRTEM for films of this thickness (~ 25 nm), and HTREM images acquire data on a very small volume fraction of the material. Voids larger than 5 nm may exist in the material but may not have been captured by the field of view of the microscope. The relative intensity of the images has no physical meaning.
Figure 9.3 | Focal series images of a-Si films grown at 23 °C, 250 °C, and 450 °C. The contrast in the 23 °C focal series is evidence for a columnar structure with columns of ~ 5-15 nm in diameter and low-density gaps of ~ 1-2 nm. The 250 °C and 450 °C films are amorphous and show no evidence of columnar structure.

One thousand nanodiffraction patterns were collected using the parameters in Chapter 8.1 for FEM analysis. Figure 9.4 shows the averaged $I(k)$ spectra for each sample. $I(k)$ quantifies the SRO of the materials. The main peaks in averaged spectra lie at 3.09, 3.09, and 3.05 nm$^{-1}$ for the 23 °C, 250 °C, and 450 °C films, respectively, with peak widths of 0.46, 0.49, and 0.42 nm$^{-1}$, respectively. The lack of significant differences in these data indicate that the interplanar distances in the samples are similar. The 23 °C and 250 °C data are not appreciably different from the 450 °C data, suggesting that $I(k)$ is insensitive to the nanocrystals present in the 450 °C film. The intensity at higher $k$ is attenuated due to atomic scattering factors which fall off as $k^4$, reducing the intensity of the high-$k$ peak. The magnitudes of the peaks vary slightly due to film thickness, but little quantitative information is available from the peak intensities.
Figure 9.4 | $I(k)$ spectra for a-Si films grown at 23 °C, 250 °C, and 450 °C. There are no meaningful differences in the data which suggests that all three films have similar SRO.

Figure 9.5 shows FEM data for the three films. $V(k)$ for the 23 °C film is similar to previously reported a-Si FEM results with peaks at 3.1 nm$^{-1}$ and 5.5 nm$^{-1}$ [151,262–264]. Previous FEM results are most consistent with a paracrystalline structural model of a-Si with diamond-cubic nanoclusters embedded in the amorphous network. The peak at 3.1 nm$^{-1}$ arises from the $<111>$ reflection in diamond-cubic silicon, and the $<220>$ and $<311>$ reflections merge to give rise to the peak at 5.5 nm$^{-1}$. However, the 250 °C and 450 °C films show an additional peak in $V(k)$ at 2.8 nm$^{-1}$, and the allowed diamond-cubic silicon reflections cannot explain this low-$k$ peak. To our knowledge, this is the first demonstration of a-Si with MRO structure different from paracrystalline diamond-cubic a-Si.
9.3 a-Si Discussion

The peak in $V(k)$ at lower $k$ must arise from a larger interatomic distance than the peaks at higher $k$. There are no diffraction peaks in diamond-cubic Si with reflections below 3.1 nm$^{-1}$, so the peaks in $V(k)$ likely come from a different crystal structure embedded in the a-Si matrix. After analyzing the diffraction features of many phases of c-Si, and the structure most consistent with the peaks in $V(k)$ is a Si$_{24}$ [269] crystal with 8-atom rings (see Figure 9.6). These 8-atom rings are larger than the 4-, 5-, and 6-atom rings present in typical paracrystalline a-Si [111] and allow for diffraction features at lower $k$. The Si$_{24}$ crystal was synthesized at high pressure with Na atoms embedded in the crystalline matrix inside the 8-atom Si rings. The material was brought to room pressure, and the Na atoms were removed from the crystalline matrix using thermal degassing [269]. The resulting crystal is stable at room temperature and pressure, and the voids left by the Na atoms leave 8-atom Si rings. It is unlikely that a high-pressure phase of c-Si crystallized at room temperature and pressure, but we believe 8-atom rings, which cause the diffraction at low $k$ in Si$_{24}$, are also causing the diffraction in the 250 °C and 450 °C films studied here.

Preliminary doppler broadening spectroscopy (DBS) results (collected by the Hellman lab and other groups) show evidence for small voids in the films, ranging from vacancy-size to 20 nm.
The existence of 8-atom rings is consistent with the DBS results because the empty spacing inside the 8-atom rings can be interpreted as the smallest sized voids in the material. FEM measurements cannot identify voids in amorphous materials, and HRTEM measurements quantify very small volumes of the material so voids may go unseen.

Figure 9.6 | The Si$_{24}$ structure in Ref. [269] contains 8-membered rings. Simulated $V(k)$ of this c-Si structure has diffraction features near the peaks in $V(k)$ for the 250 °C and 450 °C a-Si films studied here.

In order to ensure the EELS signal from the SiN grids would not interfere with the EELS signal from the a-Si thin films, we measured the plasmon peak positions of two SiN grids, one as-received and one annealed at 450 °C. Figure 9.7 shows the plasmon peak of the SiN grids measured at multiple locations on the sample. The SiN plasmon peak positions do not change with temperature and have a linearly increasing signal near the a-Si plasmon peak position at 16.6 eV, making the a-Si signal easily differentiable.
Figure 9.7 | The plasmon peaks of two SiN grids, one as-received (blue, yellow, and green curves) and one annealed at 450 °C (red and purple curves). The plasmon peak positions do not change with temperature.

EELS measurements of the three a-Si thin films revealed no significant change in average atomic distance. The average plasmon peak position for the three samples was 16.57 eV and relative changes were +0.18%, +0.48%, and -0.72%, respectively, with an error of ~0.1% (see Figure 9.8). These results do not show a significant difference in average electron number density between the three films and therefore do not provide structural evidence for the changes in the FEM signal of the room temperature and high temperature films. The 450 °C film has a slightly lower local electron density than the other two films, but not only is the difference small in comparison to a 5-10% change of bulk density, but the local density change here is opposite that of the bulk density changes measured by the Hellman group.
Figure 9.8 | The mean plasmon peak position of the three a-Si thin films calculated using multiple EELS measurements. Error bars are the standard deviation of the plasmon peak positions from the measurements. Our results agree with measurements on standard a-Si, which has a plasmon peak at 16.6 eV.

9.4 a-Si Summary

Three a-Si thin films grown by the Hellman lab at UC Berkley have large changes in density. We characterized the films using FEM and EELS techniques to study the materials’ structures. We found no evidence for local changes in density, measured using EELS, so the bulk density changes are likely due to voids. This is supported by DBS measurements performed by other groups. The two films grown above room temperature at 250 °C and 450 °C have MRO, measured using FEM, unlike other a-Si. a-Si typically has a paracrystalline structure with diamond-cubic subcritical crystallites embedded in an amorphous matrix. We show evidence for MRO in the 250 °C and 450 °C thin films that is larger than the typical 6-atom rings and hypothesize that 8-atom rings exist in these films, potentially in the form of subcritical crystallites that replace the diamond-cubic structure. Additional analysis is being conducted by the Hellman group and data from many experiments are being combined to tell a story about the structure of these films.
10 Looking Forward: Comments on Future Work

10.1 Generating Metallic Glass Models with Accurate Medium-Range Order

The HRMC models used in this work are likely subject to inaccuracies due to the small size of the bounding box. In HRMC, one nanodiffraction volume is used to estimate an FEM experiment in which thousands of nanodiffraction patterns measure the structure of the material. This discrepancy leads to the differences in structure obtained over thousands of nanodiffraction patterns being constrained to a single-pixel volume in the simulations. This may result in, for example, elevated strain levels in the atomic structure as the length scale between different types of MRO is constrained. It is currently impossible to generate MG models with realistic MRO using MD quenching. The cooling rates needed to quench large systems fast enough to have realistic MRO are orders of magnitude lower than is currently achievable using modern hardware, even using potentials that approximate the physics of atomic interactions.

StructOpt is an attempt to improve the accuracy of simulated MG models by incorporating the best aspects from various simulation algorithms. First, StructOpt’s genetic algorithm enables the sampling of diverse areas of configuration space and atomic modifications can leap energetic boundaries that may be impossible using a purely kinetic approach; second, locally-stable configurations are guaranteed because the conjugate gradient minimization forces StructOpt to only consider inherent structures; and third, experimental constrains such as FEM data encourage atomic structures that are consistent with experimental data measured from real samples (see Chapter 3.5 for details). The faster sampling of the configuration space and the parallelization capabilities of StructOpt enable larger models to be simulated in the same amount of wall-clock time as current HRMC simulations. Larger models are beneficial because they are likely to reduce small-size effects, such as those of strain due to competing MRO, and are therefore more likely to be lower in energy and have less disorder due to simulation inaccuracies. These larger models with
less disorder will simplify the search for MRO in MGs because the correlations between relative atom positions will be stronger.

10.2 Short-Range Order Structure Abstractions of All Metallic Glasses

With the identification of the BSAP in Pd-Si, we have shown that the structural precursors to the glass transition exist in both metal-metalloid and metal-metal glasses. That suggests the hypothesis that all MG systems have one or more SRO structure motifs that arrest the structure of the supercooled liquid. Identifying all of the motifs that play the same role in the glass transition in various MG systems (for which accurate energetic potentials are available) would be a major stepping stone in the quantification of MG structure. The various systems would include metal-rare-earth (Al-La and Al-Sm), metal-metal (Al-Cu, Al-Zr, Al-Ag, Cu-Zr, Zr-Pt, and Ni-Zr), metal-metalloid (Ni-P), and Mg-based glasses (Mg-Cu, Mg-Ti, and Mg-Yi). The different atomic size ratios and bonding characteristics in the systems may lead to different preferred motifs. There are a number of useful consequences of identifying one or more motifs in each of these systems that contributes to the glass transition in the same manner as BSAP and icosahedra. For example, a) we will have shown that the structural basis for the dramatic slowdown in atom dynamics near the glass transition arises from the same physics for all MGs, b) the set of motifs that contributes to the glass transition for all MGs will likely provide a subset of local structures that control properties such as GFA, c) predicting the GFA of MGs without performing expensive simulations or synthesis experiments will become simpler, and d) the property-controlling motifs will provide a mechanism for comparing and contrasting the structure and properties in MG systems with different structural order.

In addition to identifying property-controlling motifs in MG systems, motif extraction can identify all of the statistically significant local structures. By studying many MG systems, all the statistically significant local structures in MGs could be identified. Combining all of these motifs
into one superset of motifs (after removing duplicates) would provide a basis set for the structure of all MGs. This would be a significant step forward in the field of MG structure because it would allow all MGs to be compared to one another using the same structural description, i.e. comparing the SRO of each MG model to the same set of motifs. Identifying the statistically significant local structures in all MGs is straightforward (assuming accurate energetic potentials exist), but selecting the set of motifs to form a basis set of local structures to describe all MGs is difficult. This difficulty arises because the problem is poorly defined and there are no clear cutoffs for what determines whether or not two motifs are dissimilar enough to be considered distinct structures.

Lastly, an accurate quantification of SRO structure in MGs would likely enable better MRO quantification. The study of MRO as connections of SRO clusters has had some success using topological descriptions of SRO [133,140,194,223,234,270], but it is not clear whether or not the spatial correlations can be attributed to geometric constraints rather than unexpected preferential connections. A geometric description of SRO may provide an alternative description of SRO with stronger spatial correlations, such as that seen in Figure 7.12.

10.3 Quantifying Disorder in the Local Structure of Metallic Glasses

Motif extraction is better able to identify motifs when the clusters “belonging to” the motif are well-ordered and populous. Motif extraction identifies statistically significant clusters with the assumption that the clusters being analyzed have one or more underlying structures, and that the differences in clusters that arise from the same underlying structure are due to disorder. For the remainder of this discussion, the underlying structures that give rise to similar clusters are called prototypes. In the best-case scenario, motif extraction will derive motifs that are identical to the prototypes. For example, in the case of a perfect crystal, the motifs are identical to the prototypes because 1) the disorder of the clusters is negligible and 2) there are many clusters with the same structure (given a model with many unit cells). As more disorder is introduced into the system,
such as in grain boundaries or amorphous materials, the disorder of each cluster increases. As the disorder increases, more clusters are needed to define the distribution of atom positions around the atom positions of the prototype, and therefore more clusters are needed for motif extraction to identify a motif identical to the prototype. If two prototypes are structurally similar (quantified via PPM [191]) and the disorder of the clusters that arise from the two prototypes is strong, then the clusters from the two prototypes may be indistinguishable. In this case, motif extraction will identify only one motif even when two unique prototypes give rise to the group of similar clusters.

Quantifying the disorder of clusters with respect to the motif to which they are most similar will improve the theory behind motif extraction. Currently, there are only imprecise ways to measure the accuracy of the motifs identified by motif extraction. A thorough quantification of the disorder of clusters similar to a motif will facilitate a functional definition of disorder between a cluster and its motif, e.g. $D_{\text{cluster}} = f(\text{cluster}, \text{motif})$. After $D_{\text{cluster}}$ is calculated for every cluster assigned to a motif, the disorder of the motif could be defined as the average of $D_{\text{cluster}}$ for all clusters assigned to the motif. The disorder of each motif can be used as a quantitative metric of precision for how well motif extraction identified the motifs.

In addition, and more physically relevant, a thorough understanding of the disorder of clusters will provide a deeper understanding of MG structure. The disorder in a glass is correlated with its entropy and therefore with its cooling rate. Simulations on model glasses [271] show that glasses quenched at slow cooling rates have larger domains of locally-favored structures (also known as preferred structures). As a result, glasses quenched at lower cooling rates tend to have less disorder. With a quantitative description of disorder, we can better define the disorder of a simulated model independent of cooling rate or entropy. This will open the door for a new set of structure-property metrics based on the structural disorder of a system or of a motif. For example, one metric may correlate the structural disorder of a motif with a property of the local structure,
such as plastic deformation. We already know that some prototypes are inherently more disordered than other motifs. For example, the fcc-like motifs in the HRMC glasses studied in this work are less disordered than other motifs (see, e.g., Figure 8.8).

10.4 A Possible Description of Defects in Metallic Glasses

The abstract description of MG structure as arising from prototype local structures with disorder suggests an enticing description for intrinsic defects in MGs. That is, defects are atoms with a local structure that is dissimilar to all prototypes found in the glass. Given a superset of motifs that fully describe the SRO structure of all MGs, the identification of such defects is plausible. Their identification may lead to a better understanding of properties such as plastic deformation in shear transformation zones, analogous to defects controlling mechanical properties in crystals. Alternatively, interstitials and vacancies in MGs can be identified by searching for clusters with high similarity (quantified via PPM [191]) to motifs whose CN is one higher or one lower than the cluster. Defects may be most visible in glasses that have undergone local deformation, e.g. via shear or ion radiation. Work on defects identified via PPM is currently very preliminary but shows promise. Constructing a robust definition of a defect has proven particularly difficult.
11 Conclusions

Chapter 3 introduced new software called StructOpt to generate model structures of disordered materials that agree with experimental data and have low energy, as well as a new structure identification technique called motif extraction that identifies the statistically significant local structures in disordered materials. Motif extraction is applied to Zr-Cu-Al, Pd_{82}Si_{18}, and Al_{92}Sm_{8} MGs models generated via MD and HRMC simulations. Chapter 4 uses topological structure metrics to compare two glasses with different GFA in the Zr-Cu-Al system, revealing that subcritical fcc-like MRO exists at the nanometer scale, and better glass forming alloys can be creating by destabilizing crystal-like SRO and MRO. An MD glass with a similar composition is studied in Chapter 6.1-6.2 to test the motif extraction technique. Motif extraction also revealed a new hierarchy of structures as a function of coordination number that is focused around icosahedral geometries, which are dominant in metal-metal glasses. In Chapter 6.3, an analogous hierarchy of structures is found in HRMC models of Zr_{50}Cu_{35}Al_{15} that focuses around fcc geometries. This suggests that one or two motifs may fundamentally dominate the structure of both glassy and crystal-like SRO in MGs.

Chapter 5 introduces Pd_{82}Si_{18} as a metal-metalloid glass that is used as a comparator to the Zr-Cu-Al glasses studied. We see that topological structure descriptors are unable to explain the changes in structure measured by FEM, which is consistent with previous results showing that topological structure descriptors cannot account for significant changes in structure in Pd_{82}Si_{18}. Chapter 7 uses motif extraction to study the structure of the Pd_{82}Si_{18} glasses. The motifs identified are distributed heterogeneously in the models, in contrast to the topological results. The (SRO) motifs are unable to explain the changes in structure seen in FEM measurements, which suggests that the SRO in the glasses may be indistinguishable and instead the MRO controls the changes in FEM measurements.
Chapter 8 presents an analysis of two \text{Al}_92\text{Sm}_8\ MGs created using different synthesis techniques. HRMC simulations and the motif extraction technique reveals MRO analogous to metal-metal and metal-metalloid glasses, including the fcc-like hierarchy of order, illustrating that fcc-like close-packed order may be ubiquitous in MG systems. The structures of the two \text{Al}_92\text{Sm}_8 glasses are distinguished by a higher fraction of fcc order in the glass synthesized using mechanical rolling, compared to the glass to synthesized via melt-spinning. Finally, Chapter 9 reports experimental work identifying a new type of MRO structure in a-Si thin films. The new MRO is consistent with larger 8-atom rings rather than the 6-atom rings that are typically found in the structure of a-Si.
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