ATOMISTIC MODELLING AND PREDICTION OF GLASS FORMING ABILITY IN BULK METALLIC GLASSES

By

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science
Materials Science and Engineering
University of Toronto

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Masters of Applied Science
Materials Science and Engineering
University of Toronto
2015

Abstract

Atomistic modeling was conducted to investigate kinetics, thermodynamics, structure, and bonding in Ni-Al and Cu-Zr metallic glasses. This work correlates GFA with the nature of atomic-level bonding and vibrational properties, with results potentially extensible to the Transition Metal – Transition Metal and Transition Metal – Metalloid alloy classes in general. As a first step in the development of a liquid-only GFA tuning approach, an automated tool based on molecular dynamics has also been created for the broad compositional sampling of liquid and glassy phase properties in multicomponent alloy systems. Its application to the Cu-Zr alloy system shows promising results, including the successful identification of the two highest GFA compositions, Cu_{50}Zr_{50} and Cu_{64}Zr_{36}. Overall, the findings of this work highlight the critical importance of incorporating more complex alloy-specific information regarding the nature of bonding and ordering at the atomic level into such an approach.
Acknowledgments

First and foremost, I’d like to extend my thanks and gratitude to Professors Chandra Veer Singh, Steven J. Thorpe, and Donald W. Kirk for their persistent guidance, mentorship, and support throughout the duration of my graduate studies. The work of this thesis and my experience throughout its completion would not have been possible, nor as fulfilling, without their unified supervision and active involvement.

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<th>Description</th>
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<tbody>
<tr>
<td>BMG</td>
<td>Bulk metallic glass</td>
</tr>
<tr>
<td>GFA</td>
<td>Glass forming ability</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>IS</td>
<td>Inherent structure</td>
</tr>
<tr>
<td>GIS</td>
<td>Generalized inherent structure</td>
</tr>
<tr>
<td>CNT</td>
<td>Classical nucleation theory</td>
</tr>
<tr>
<td>CFM</td>
<td>Coupled flux model</td>
</tr>
<tr>
<td>TM-TM</td>
<td>Transition Metal – Transition Metal</td>
</tr>
<tr>
<td>TM-M</td>
<td>Transition Metal – Metalloid</td>
</tr>
<tr>
<td>NVE</td>
<td>Constant particle number, volume, and energy</td>
</tr>
<tr>
<td>NVT</td>
<td>Constant particle number, volume, and temperature</td>
</tr>
<tr>
<td>NPT</td>
<td>Constant particle number, pressure, and temperature</td>
</tr>
<tr>
<td>µVT</td>
<td>Constant chemical potential, volume, and temperature</td>
</tr>
<tr>
<td>CN</td>
<td>Coordination number</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units [SI]</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_B)</td>
<td>J K(^{-1})</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>(h)</td>
<td>J s</td>
<td>Plank’s constant</td>
</tr>
<tr>
<td>(\beta)</td>
<td>J(^{-1})</td>
<td>Thermodynamic beta (inverse temperature)</td>
</tr>
<tr>
<td>(\sigma_E)</td>
<td>J(^2)</td>
<td>Energy variance under thermodynamic fluctuations</td>
</tr>
<tr>
<td>(C_v)</td>
<td>J T(^{-1})</td>
<td>Constant volume heat capacity</td>
</tr>
<tr>
<td>(C_p)</td>
<td>J T(^{-1})</td>
<td>Constant pressure heat capacity</td>
</tr>
<tr>
<td>(\alpha_T)</td>
<td>m(^3) T(^{-1})</td>
<td>Isothermal expansion coefficient</td>
</tr>
<tr>
<td>(B_T)</td>
<td>Pa</td>
<td>Bulk Modulus</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>-</td>
<td>Gruneisen parameter</td>
</tr>
<tr>
<td>(N)</td>
<td>-</td>
<td>Number of atoms</td>
</tr>
<tr>
<td>(V)</td>
<td>m(^3)</td>
<td>Volume</td>
</tr>
<tr>
<td>(T)</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>(P)</td>
<td>Pa</td>
<td>Pressure</td>
</tr>
<tr>
<td>(G)</td>
<td>J</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>(A)</td>
<td>J</td>
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</tr>
<tr>
<td>(E)</td>
<td>J</td>
<td>Internal energy</td>
</tr>
<tr>
<td>(S)</td>
<td>J/K</td>
<td>Entropy</td>
</tr>
<tr>
<td>(\Omega)</td>
<td>-</td>
<td>Microcanonical (NVE) Partition Function (Multiplicity)</td>
</tr>
<tr>
<td>(Z)</td>
<td>-</td>
<td>Canonical (NVT) Partition Function</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>-</td>
<td>Isothermal-Isobaric (NPT) Partition function</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>$\Xi$</td>
<td>Grand Canonical Partition Function</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>Canonical Configurational Partition Function</td>
<td></td>
</tr>
<tr>
<td>$S_c$</td>
<td>J K$^{-1}$ Configurational entropy</td>
<td></td>
</tr>
<tr>
<td>$H(x^{(6N)})$</td>
<td>J Classical Hamiltonian Function</td>
<td></td>
</tr>
<tr>
<td>$\Phi(r^{(3N)})$</td>
<td>J potential energy function</td>
<td></td>
</tr>
<tr>
<td>$r^{(N)}$</td>
<td>m 3N-dimensional atomic coordinates</td>
<td></td>
</tr>
<tr>
<td>$p^{(N)}$</td>
<td>kg m s$^{-1}$ 3N-dimensional atomic momenta</td>
<td></td>
</tr>
<tr>
<td>$x^{(6N)}$</td>
<td>- 6N-dimensional phase space coordinate</td>
<td></td>
</tr>
<tr>
<td>$v$</td>
<td>m s$^{-1}$ 3-dimensional atomic velocity</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td>N 3-dimensional atomic force</td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>Kg Atomic mass</td>
<td></td>
</tr>
<tr>
<td>$r^{(N)}_\alpha$</td>
<td>- Stable packing configuration in 3N-dimensional space</td>
<td></td>
</tr>
<tr>
<td>$R_\alpha$</td>
<td>- Quench regions / basins / inherent structures</td>
<td></td>
</tr>
<tr>
<td>$\lambda_D$</td>
<td>m De-Broglie wavelength</td>
<td></td>
</tr>
<tr>
<td>$\beta^*$</td>
<td>s$^{-1}$ Growth-rate for critically sized clusters</td>
<td></td>
</tr>
<tr>
<td>$Z_f$</td>
<td>- Zeldovich factor</td>
<td></td>
</tr>
<tr>
<td>$f$</td>
<td>- Fill-fraction</td>
<td></td>
</tr>
<tr>
<td>$\Delta G^*$</td>
<td>J Nucleation free energy barrier</td>
<td></td>
</tr>
<tr>
<td>$n^*$</td>
<td>- Critical nuclei size</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{ls}$</td>
<td>J m$^{-2}$ Liquid-crystal interfacial free energy</td>
<td></td>
</tr>
<tr>
<td>$I^{ss}$</td>
<td>s$^{-1}$ V$^{-1}$ Steady-state nucleation rate per unit volume of liquid</td>
<td></td>
</tr>
<tr>
<td>$Y^{ss}$</td>
<td>m s$^{-1}$ Steady-state crystal planar-growth velocity</td>
<td></td>
</tr>
<tr>
<td>$g(\omega)$</td>
<td>- Vibrational density of states</td>
<td></td>
</tr>
<tr>
<td>$\bar{v}$</td>
<td>m$^3$ Specific volume</td>
<td></td>
</tr>
<tr>
<td>$\Delta \mu_{LC}$</td>
<td>J mol$^{-1}$ Liquid-crystal partial molar Gibbs free energy difference</td>
<td></td>
</tr>
<tr>
<td>$\Delta h_{LC}$</td>
<td>J mol$^{-1}$ Liquid-crystal partial molar enthalpy difference</td>
<td></td>
</tr>
<tr>
<td>$\Delta S_{LC}$</td>
<td>J K$^{-1}$ mol$^{-1}$ Liquid-crystal partial molar entropy difference</td>
<td></td>
</tr>
<tr>
<td>$t_{x}^{ss}$</td>
<td>s Time for crystallization up to cutoff crystal fraction x</td>
<td></td>
</tr>
<tr>
<td>$T_{nose}$</td>
<td>K Nose temperature in T-T-T crystallization profile</td>
<td></td>
</tr>
<tr>
<td>$T_m$</td>
<td>K Melting point</td>
<td></td>
</tr>
<tr>
<td>$T_l$</td>
<td>K Liquidus temperature</td>
<td></td>
</tr>
<tr>
<td>$T_g$</td>
<td>K Glass transition temperature</td>
<td></td>
</tr>
<tr>
<td>$T_{rg}$</td>
<td>- Reduced glass transition temperature</td>
<td></td>
</tr>
<tr>
<td>$T_{MC}$</td>
<td>K Mode coupling temperature</td>
<td></td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>- Gamma value</td>
<td></td>
</tr>
<tr>
<td>$\Delta T_x$</td>
<td>K Temperature difference between glass transition and onset crystallization (from below)</td>
<td></td>
</tr>
<tr>
<td>$m$</td>
<td>- Kinetic fragility parameter</td>
<td></td>
</tr>
<tr>
<td>$D^*$</td>
<td>- VFT Strength Parameter</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>K VFT effective activation energy</td>
<td></td>
</tr>
</tbody>
</table>
\( T_0 \) K  VFT divergence temperature
\( \eta \) Pa s  Viscosity
\( D \) m\(^2\) s\(^{-1}\)  Atomic Diffusivity
\( \tau \) s  Relaxation time
\( P \) moles m\(^{-3}\)  molar density
\( \text{PSD} \) m\(^2\) s\(^{-1}\)  Velocity power spectral density
\( p_{\alpha\beta} \) Pa m\(^{-3}\)  Symmetrized traceless Virial stress tensor
\( \sigma_{\alpha\beta} \) Pa m\(^{-3}\)  Virial stress tensor
\( g_{\alpha\beta}(r) \) -  Partial radial distribution function
\( \alpha_p \) -  Warren-Cowley parameter
\( (\Delta\mu)_{T_g} \) J mol\(^{-1}\)  Liquid-crystal partial-molar free energy difference at \( T_g \)
\( \omega \) s\(^{-1}\)  Vibrational frequency
\( q \) m\(^{-1}\)  Wave-vector
\( k \) m  Interatomic force-constant (spring-constant)
\( C_{\alpha\beta} \) -  Bond correlation function
\( \bar{\rho}_i \) moles m\(^{-3}\)  Mean local electron density
\( \rho_{s_j} \) moles m\(^{-3}\)  Electron density function
\( \varphi_{s_i s_j} \) J  EAM pair-interaction potential
\( F_{s_i} \) J  EAM embedding energy
Chapter 1

1 Introduction

Unlike conventional crystalline alloys, bulk metallic glasses exhibit little to no long range structural order at the atomic level, with structures essentially consisting of random, tightly packed clusters of atoms. The first experimental evidence of metallic glasses arose in 1959 when Klement, Williams, and Duwez were able to fabricate Au$_{75}$Si$_{25}$ metallic glass by splat quenching the metallic liquid melt onto a cold plate, resulting in rapid quenching at a rate of $10^5 - 10^6$ K s$^{-1}$ and thereby inhibiting crystallization [1]. While such methods provided a proof of concept, widespread application of amorphous metals on a consumer level was largely confined to thin films due to the kinetic demands of rapid heat transfer. As of today, a number of metallic glasses have been discovered which allow for fabrication methods involving far lower critical cooling rates [2], and thus can be formed in much larger dimensions. These bulk metallic glasses (BMGs) often share the common characteristics of being multi-component alloys, rich with transition metals (and noble metal - metalloid species) at or near deep eutectic compositions.

1.1 Background

BMGs are now being considered for use in a number of consumer and specialty device applications, with interest peaked by their unique set of mechanical and magnetic properties [3][4][5]. Currently under investigation is the application of BMGs for use in the pivot-flexure component of orthogonal quadrupole responders in Gedex Inc.’s next generation room temperature airborne gravity gradiometers (used for mining and mineral exploration purposes). The appeal of specific BMG’s being the high strength, high linear elastic deflection limits, low loss coefficients, and low magnetic susceptibilities characteristic of some glassy alloys operating at room temperature. While the disordered nature of BMGs is ultimately responsible for their unique set of mechanical and magnetic properties, an unfortunate byproduct of said disorder is an increased degree of complexity and general lack of simplifying assumptions for the modeling and prediction of underlying compositional dependencies. Slight variations in composition (often as little as a single atomic percent) and processing conditions (cooling rate, impurity and oxygen content, melt duration and degree of overheating, mold surface smoothness, suction/extrusion
rates etc.) can dramatically alter underlying thermodynamic, kinetic, structural, and physical properties of multicomponent melts and glasses. Of particular importance is the significant compositional sensitivity of glass forming ability and crystallization kinetics. Currently, a key focal point of BMG research is the search and discovery of key parameters influencing glass forming ability, identifying how they are reflected in structural, thermodynamic, and kinetic properties, and studying how these properties can subsequently be tuned in a controlled manner. Many approaches have been proposed for the compositional tuning of BMGs [6-12], however as of yet, a robust method capable of fine compositional tuning for the optimization of glass forming ability (GFA) in multicomponent alloys has not been reported.

1.2 Motivation

Despite significant recent advances in the field of glass sciences, a clear-cut design approach for the compositional tuning of glass forming ability in BMGs has yet to be identified. The vast compositional spaces needed to be explored, in conjunction with the fine compositional sensitivity observed in many multicomponent alloy systems makes the experimental identification of high GFA alloys an incredibly arduous task. Current computational and analytic tuning methods are severely limited in their applicability due to a number of non-trivial factors. Many of the identified GFA indicators and influencing factors are not single phase properties and often depend on properties of the disordered and crystallizing phases and/or the interface between the two. In complex multi-component systems, the crystallizing phase is rarely known before hand, with the crystallization pathway leading to the final equilibrium phase more often than not being a multi-step process involving several (also likely unknown) intermediate (polymorphic) metastable phases. Without detailed knowledge of equilibrium and non-equilibrium phase diagrams, these considerations raise the important question of whether fundamental limitations exist on the practicality of a computational (or experimental) method capable of rapid, accurate, and compositionally robust GFA tuning. Many of the existing GFA tuning methods and predictive indicators (even those relying upon only single phase properties) exhibit a significant lack of robustness, with their efficacy often being highly dependent upon the alloy class in question, or otherwise being restricted to specific compositional domains. These issues can to a great extent be attributed to a general lack of understanding of underlying bonding differences at the atomic level.
With the improvement of interatomic potentials and the steady advancement of molecular dynamics techniques, current simulations methods allow for the sampling of liquid, supercooled, and glassy phase (albeit, rapidly quenched) properties of multicomponent alloys with little to no prior knowledge of the underlying system. Since general correlations between glass forming ability and simple parameters such as the atomic size ratio, amorphous phase packing efficiency, and liquid fragility exist, the development of a rapid and compositionally robust tuning approach reliant upon disordered phase properties alone may be possible. For this advance, the identification of GFA indicators and influencing factors relying solely upon properties of the disordered phase is of utmost importance. Equally important is the investigation of the inherent limitations of existing GFA predictive indicators, the underlying causes for their breakdown in certain alloy systems or beyond certain compositional domains, and potential methods for accounting or correcting for these factors. This requires a detailed understanding of the nature of bonding in different alloy classes, and how these general differences are subsequently reflected in the degree and nature of short and medium-range ordering, in the energy landscape and structural relaxation properties, and ultimately the mechanisms through which crystal nucleation and growth occur. Ideal in this respect is the investigation of the atomic level factors influencing the rapid crystal nucleation and growth rates of the Transition Metal – Metalloid (TM-M) Ni$_{50}$Al$_{50}$ system in comparison to the Transition Metal – Transition Metal (TM-TM) Cu$_{50}$Zr$_{50}$ alloy, an apparently anomalous result which largely persists to be a source of confusion in the BMG community.

1.3 Thesis Objectives

In this thesis, the underlying bulk and atomic level influences of glass forming ability in multicomponent metallic glasses, and the prospect of a rapid and robust computational tuning approach using molecular dynamics simulation methods are explored. Accordingly, the following thesis objectives are presented:

1) Explore and identify the key influencing factors and predictive indicators of glass forming ability in multicomponent alloy systems

2) Investigate the atomic-level influencing factors of glass forming ability in Cu-Zr and Ni-Al metallic glasses
3) Investigate compositional dependencies of short-range ordering, transport properties, and glass forming ability in the Cu-Zr system

4) Develop an automated computational tool for the broad-compositional search and analysis of thermodynamic, kinetic, and structural properties in multicomponent glasses

1.4 Thesis Organization

Chapter 2 outlines the fundamental theory of supercooling thermodynamics, the glass formation process, the evolution of transport properties, and crystallization kinetics, ending with a literature review of the best identified predictive indicators for glass forming ability in multicomponent alloys. In Chapter 3, methodology and computational details regarding molecular dynamics simulations and property extraction methods utilized in this study are presented. Chapter 4 provides a detailed analysis of thermodynamic, kinetic, and structural properties of equimolar Ni-Al and Cu-Zr metallic glasses, with a primary focus being the investigation of GFA anomalies, the evaluation of the predictive efficacy of various indicators, and the exploration of underlying connections to atomic-level bonding, ordering, and vibrational properties. In Chapter 5, the development and capabilities of an automated glass analysis tool are summarized, with results of its application to the investigation of broad-compositional trends in underlying short-range structural properties, the kinetic fragility parameter, and glass forming ability in the Cu-Zr system being presented. Lastly, overall results and conclusions of this work are summarized in Chapter 6.
Chapter 2

2 A Review of Glass Formation and Crystallization Kinetics Theory

In order to understand the fundamental factors influencing glass forming ability, it’s important to first gain a deep physical understanding of the supercooling process and the nature of the glassy state. The rapid quenching process underlying glass formation adds great complexity to the problem at hand, resulting in general property dependencies of the liquid melt and glassy phases on both composition and thermal history. In contrast to the thermally stable high temperature liquid phase or the low temperature equilibrium crystalline phase, this underlying thermal history dependence can be seen to reflect the fundamentally non-equilibrium nature of the glassy state. The supercooled liquid phase exists in a state of metastable equilibrium at small to moderately undercooled temperatures. Considering the intrinsic connection between glass forming ability and the thermodynamic phase stability of the liquid and glassy phases, it is vital that these concepts are concretely defined and well understood.

2.1 Thermodynamic Stability, Metastability, and Instability

At a fundamental level, a phase or macrostate can be understood to encompass some characteristic sub-volume of configurational space, with its respective thermal stability being determined by its total corresponding occupation probability under random state sampling of the equilibrium ensemble. With this in mind, the identification of the most thermodynamically stable (equilibrium) state/phase of a system can be equivalently framed in terms of a problem of probability maximization, or alternatively, one of Free Energy minimization. From this perspective, the standard thermodynamic condition for process spontaneity (a negative Helmholtz free energy change, $\Delta A_{1 \rightarrow 2} < 0$) under NVT operating conditions can be viewed to be a simple statement that spontaneous processes evolve to other more probabilistically favoured, lower free energy states. The equilibria of two distinct states or phases can similarly be interpreted in terms of the condition of equal system occupational probabilities or free energies. Under different operating conditions, the identification of the most thermodynamically stable state/phase can similarly be framed in terms of probability maximization under the various thermodynamic ensembles, or alternatively, in terms of entropy (S) maximization under NVE
conditions, Gibbs Free Energy (G) minimization under NPT/μVT conditions, or even in terms of Internal Energy (E) minimization under NVS isentropic conditions.

In order to apply the above principles to the understanding of phase equilibria and transitions in general, it is important to introduce the concept of an order parameter as a means of distinguishing between different phases. By definition, an order parameter can be any thermodynamic average \( \langle X(r^{(N)}, p^{(N)}, V) \rangle \) (corresponding to some physical observable property) which serves to distinguish two distinct phases, which may be as simple as the total system density, for example, or perhaps related to more complex symmetry properties of the underlying system. First order phase transitions such as the liquid-to-crystal phase transition experienced near the melting point \( T_m \) of metallic alloys are fundamentally characterized by the presence of some latent heat, translating to a discontinuity in some standard thermodynamic physical observable (or order parameter) such as the internal energy, \( \bar{E} \). A discontinuity in \( \bar{E} \) or some other standard first order thermodynamic physical observables (such as volume) can be seen to correspond to a discontinuity in a first order partial derivative of the free energy or Partition Function (i.e. see (A.9) in the appendices), hence the “first order” classification of the solid-liquid phase transition. Truly discontinuous phase transitions occur strictly under equilibrium conditions at the thermodynamic limit \( (N \to \infty) \) where kinetics is not a factor. In practice, however, first order phase transformations (such as the solid-liquid phase transition occurring during crystallization from the liquid melt) occur over some finite time duration, with kinetics often being limited by the requirement for large length-scale chemical diffusion and the occurrence of statistically rare structural re-ordering events. With this in mind, the phase transformation process in general is seen to extend over some finite temperature window below the equilibrium melting temperature. In certain cases, the phase transformation process may be bypassed all together, with the liquid existing in a state of metastable equilibrium within the supercooled liquid domain.

The condition of metastable thermodynamic equilibrium can be understood to require local phase stability with respect to small (local and global) perturbations in underlying system properties and parameters. Expressing the system free energy \( G \) at temperature \( T \) and pressure \( P \) in terms of some additional structural or chemical order parameter(s), \( \langle X \rangle \), which effectively differentiate the
liquid and crystalline phases, say with $\langle X \rangle_{\text{liquid}} = X_t$, and $\langle X \rangle_{\text{crystal}} = X_c$, metastability of the supercooled liquid phase at minimum requires:

$$\frac{\partial^2 G(X)}{\partial X^2}|_{X=X_l} > 0 \quad \text{with} \quad G(X_l) > G(X_c) \quad (2.1)$$

In this respect, the supercooled liquid can be viewed to exist in a state of a local, but not global, free energy minimum. In practice, the additional requirement of a large free energy barrier:

$$\Delta G_{l\rightarrow c}^* = G(X^*) - G(X_l) \quad (2.2)$$

existing at some intermediate transition state, $X^*$, is required in order to prevent the system from freely transitioning to the crystalline phase under random equilibrium fluctuations at the given temperature and pressure. As will be discussed in the following sections, in conjunction with the thermally activated nature of crystal nucleation and growth, transport and structural relaxation properties of supercooled liquids experience a significant kinetic slowdown upon extended undercooling, allowing certain alloy systems possessing sufficiently slow crystallization rates to be kinetically “frozen” into an atomically disordered solid state, e.g. a metallic glass.

### 2.2 Energy Landscape Theory

The energy landscape perspective is considered to be one of the best conceptual frameworks for understanding the equilibrium and non-equilibrium properties of liquids and glasses. Under this formulism, the $3N$ dimensional potential energy landscape $\phi(r_1, r_2, r_3, \ldots, r_N)$ is partitioned about a discrete set of stable packing configurations, $\{r_\alpha^{(N)}\}$, where the potential energy lies at a local minimum with respect to all atomic coordinates. Within this context, system dynamics and evolution can be broadly separated into independent contributions associated with anharmonic intra-basin vibrations about local potential energy minima, and more in-frequent larger scale “basin hopping” transitions across potential energy saddle-points leading into nearby thermally accessible basins [13] (as illustrated schematically in Figure 2.1).
Figure 2.1: A simplified depiction of the potential energy landscape in multidimensional configuration space (taken from Stillinger [13])

Conceptually, this partitioning of configurational space can be understood by considering the first-order evolution equations, for which steepest descent paths are characterized by:

\[ \dot{\mathbf{r}}^{(N)} = \nabla_{\mathbf{r}^{(N)}} \phi(\mathbf{r}^{(N)}) \]  

(2.3)

Following first-order steepest descent paths, it can be shown [14] that any point in configurational space (with the exception of a discrete volume of zero measure corresponding to the set of “saddle-points” and other generalized critical points) maps to a corresponding stable packing configuration in the discrete set of \( \{ \mathbf{r}_\alpha^{(N)} \} \). All associated elements of configurational space mapping to minima \( r_\alpha \) define sub-regions, \( R(\mathbf{r}_\alpha^{(N)}) \), known as the “quench regions”, “basins”, or “inherent structures”. All inherent structure energies, \( \phi(\mathbf{r}_\alpha^{(N)}) = \phi_\alpha \), can be seen to lie somewhere in the range of \( \phi_o \leq \phi_\alpha \leq \phi_u \), where \( \phi_o \) denotes the lowest potential energy (crystalline) stable packing configuration, and \( \phi_u \) the highest. Re-expressing the configurational partition function integral as a sum over individual inherent structures, defining configurational entropy:

\[ S_c(\phi) = k_B \ln N(\phi) \]  

(2.4)
where \(N(\phi)\) is the number of distinct stable packing states within some narrow energy band about \(\phi\), and denoting the mean intra-basin vibrational free energy of associated basins, \(f(\phi, T, V)\), the probability of sampling a basin of energy \(\phi\) upon instantaneous quenching the equilibrium melt at temperature \(T\) can be shown to be given by [14]:

\[
P(\phi, T, V) = \frac{\exp\{-\beta(-S_c(\phi)T + \phi + f(\phi, T, V))\}}{Z(T, V)}
\]  

(2.5)

Where \(Z(N, T, V)\) is the canonical partition function and can be expressed as an integral over basin energies as:

\[
Z(N, T, V) = \frac{1}{N! \lambda^3} \int_{\phi_0}^{\phi_u} d\phi \exp\{-\beta(-S_c(\phi)T + \phi + f(\phi, T, V))\}
\]  

(2.6)

As usual, the Helmholtz Free Energy is defined by:

\[
F(N, T, V) = -k_B T \ln Z(N, T, V)
\]  

(2.7)

which in the thermodynamic limit (where \(N \to \infty\)) can be approximated to first order by a maximum integrand approach, resulting in the final expression for the system free energy under energy landscape theory:

\[
F(T, V) \approx \bar{\phi} - TS_c(\bar{\phi}) + f(\bar{\phi}, T, V)
\]  

(2.8)

where \(\bar{\phi}\) is the basin potential energy that maximizes the integrand, and can intuitively be understood to represent the mean potential energy expected upon instantaneous quenching from a randomly sampled equilibrium configuration at temperature \(T\) [14]. While the above conclusions are derived under the context of equilibrium statistical mechanics, the same formulism can be applied to understand thermodynamic properties of the supercooled liquid phase. In this respect, the supercooled liquid is viewed as existing in a state of metastable equilibrium within the restricted (meta-basin) sub-domain of structurally amorphous inherent structures. With this in mind, the thermodynamic stability of a given phase in general can be seen to be governed by three main factors: 1) the mean basin potential energy (or enthalpy), 2) the mean configurational entropy which is related to the logarithm of the number of distinct
accessible basins, and 3) the mean intra-basin vibrational free energy, at the given temperature and pressure. For a more in-depth overview and derivation of these results, see Appendix B.

2.3 Supercooling Thermodynamics from an Energy Landscape Perspective

Studies examining the temperature dependencies of inherent structures through energy landscape sampling have revealed that higher temperature liquid phase inherent structures are generally shallower (wider curvature, with lower transition barriers for escape) and possess higher potential energies on average than those sampled at lower temperatures \[15\][16]. In conjunction with a gradual reduction in thermal energy and the gradual evolution to deeper, lower energy inherent structures at lower temperatures, an underlying topological (continuous) phase transition is found to occur in the potential energy landscape at the Mode Coupling temperature, \( T_{MC} \) (often lying somewhere between the \( T_g \) and \( T_M \) of many liquid melts) \[17\][18]. Above this critical temperature, the nearest stationary points or generalized inherent structures (GIS) visited through means of steepest descent energy minimization are found to correspond to saddle points (potential energy Hessian at critical point possesses at least one negative eigenvalue), subsequently, diffusion and atomic transport in this region predominately occurs along unstable directions of saddles\[46\]. Below \( T_{MC} \), a topological phase transition occurs to a phase space domain whose nearest stationary points correspond to local potential energy minima (all positive energy Hessian eigenvalues). Consequently, dynamics are seen to become increasingly activated upon cooling, with phonon-like vibrational modes predominating in this low temperature phase while being absent in the high temperature phase above \( T_{MC} \). These underlying topological changes in the potential energy landscape have huge impacts on transport properties and structural relaxation times which are directly related to the ease at which the liquid can explore nearby configurations, eventually leading to a divergence in underlying relaxation times in the heavily undercooled domain. These concepts are crucial to the understanding of the evolution of transport properties, the glass transition phenomena, and the cooling rate dependence of thermodynamic and physical properties in supercooled liquids and metallic glasses.
Figure 2.2: Cooling rate and temperature dependence of a typical liquid melt’s enthalpy and volume at constant pressure. Inset illustrations on the right depict typical local potential energy landscape environments experienced at various stages of the quench. Fictive temperatures, $T_f$, and glass transition temperatures, $T_g$, are also presented for both fast and slowly quenched glasses. $T_m$ is the melting point temperature, and $T_{MC}$ is the mode coupling temperature.

For improved clarity of these concepts, an example of equilibrium and non-equilibrium cooling curves typical of a common liquid melt is presented in Figure 2.2. Comparing the blue supercooled curves extending down into the glassy phase, the dramatic changes in local landscape topology and the associated enhanced activation of dynamics in the deeply undercooled domain (below $T_{MC}$) are seen to result in an inherent non-equilibrium cooling rate dependence of standard thermodynamic properties such as the enthalpy and specific volume. A
more rapid quenching process can be viewed to prematurely “freeze” the supercooled liquid into a less thermodynamically relaxed, higher energy subset of amorphous inherent structures. In this respect, the fictive temperature, \( T_f \), of a glass is defined as the temperature at which the theoretical (metastable) equilibrium liquid would be expected to occupy the same subset of configurational space (basins) in which the glass is frozen into, which in practice is determined by the intersection of extrapolated glass and equilibrium liquid property lines. Consistent with these notions, more rapidly quenched glasses are seen to possess higher fictive and glass transition temperatures (as illustrated in Figure 2.2, with \( T_f,\text{(fast)} > T_f,\text{(slow)} \) and \( T_g,\text{(fast)} > T_g,\text{(slow)} \)).

The process of glass formation can subsequently be understood as a non-equilibrium process, intrinsically linked to the competition between internal (structural, enthalpic, etc.) relaxation times and experimental timescales governed by the cooling rate. At the glass transition temperature, internal shear/enthalpic relaxation times \( \tau_{\text{int}} \) become comparable in magnitude to experimental/observational timescales (\( \tau_{\text{int}} \approx \tau_{\text{obs}} \)). Considering that shear viscosity is proportionally dependent upon underlying shear relaxation times (\( \eta \sim \tau_{\text{rel}} \)), this condition is generally satisfied for most liquids under standard experimental operating conditions when viscosities are on the order of \( 10^{12} \) Pa-s. Hence the standard rheological definition for the glass transition temperature: \( \eta(T_g) = 10^{12} \) Pa-s. Bringing everything together, when cooling the liquid below the melting/liquidus point under equilibrium conditions, sufficient time is provided for the system to explore a representative volume of configurational space and to eventually reach an “entrance pathway” leading to the low energy, thermodynamically favorable crystalline phase. Under highly non-equilibrium cooling conditions (i.e. rapid quenching), insufficient time is provided for the system to transition to lower energy crystalline basins, with crystallization effectively being bypassed.

### 2.4 Transport Properties and Kinetics in the Liquid and Supercooled Domains

In the high temperature equilibrium liquid melt regime (\( T >> T_M \)), the availability of excess thermal energy largely overrides underlying potential energy landscape influences on dynamics, resulting in transport properties well described by the free diffusion of spherical particles. With this in mind, simple hydrodynamic treatments of particle dynamics in accordance with the Stoke-Einstein relations predict a simple inverse law relationship between shear viscosities and
diffusivities in this regime, which is largely found to hold well down into the minimally undercooled regime for the majority of liquid melts [19]:

\[
D(T) = \frac{k_B T}{6\pi b \eta(T)} \sim c \frac{T}{\eta(T)}
\]  

(2.9)

where \(D(T)\) and \(\eta(T)\) is the self-diffusivity and shear viscosity at temperature \(T\), and \(b\) is the effective hydrodynamic atomic radius. As per the standard Maxwell fluid model (or more concretely under the Green-Kubo relations in the framework of linear response theory and nonequilibrium statistical mechanics), the shear viscosity is directly related to underlying shear relaxation times, \(\eta(T) \sim \tau_{\text{shear}}(T)\). At very high temperatures, linear transport properties and corresponding relaxation times display an approximate Arrhenius law temperature dependencies under a singular effective activation energy, \(E_a\):

\[
\tau(T) \sim \exp\left(\frac{E_a}{k_B T}\right)
\]

(2.10)

However, as system dynamics become increasingly landscape influenced upon further cooling, a departure from an Arrhenius form of temperature dependency is expected in most systems. Instead, the temperature dependence of underlying relaxation and transport properties in the lower temperature liquid and supercooled melt domain is more generally described by the Vogel-Tamman-Fulcher (VFT) functional form [19]:

\[
\eta(T), \tau_{\text{shear}}(T), \tau_{\text{thermal}}(T), D^{-1}(T) \approx A \exp\left[\frac{B}{T - T_o}\right]
\]

(2.11)

where \(A, B,\) and \(T_o\) are temperature independent constants. The classification of liquids as “strong” or “fragile” serves as a useful metric quantifying the adherence of viscosity and relaxation times to the Arrhenius law functionality, with fragile liquids displaying more marked deviations from the Arrhenius form. Fragile glasses can be understood to experience a more dramatic and abrupt viscous slow-down process on approach to the glass transition temperature in the deeply undercooled liquid domain, a concept which is more clearly illustrated by the more linear \(T_g\)-scaled log-viscosity profile (known as Angell plots [20]) observed in strong glasses. In practice, the kinetic fragility parameter, \(m\), and strength parameter, \(D^*\), serve to quantify the
fragility of liquids (both defined below), with lower kinetic fragilities and higher strength parameters being reflective of less fragile / stronger liquids.

\[ m = \left( \frac{\partial \log_{10} \eta(T)}{\partial (T_g/T)} \right)_{T=T_g} \]  

\[ D^* = \frac{B}{T_0} \]  

2.5 Crystallization Kinetics

Many of the concepts discussed in the previous sections have been concerned with properties of supercooled liquids, with the implicit assumption that the disordered liquid phase exists in a state of metastable equilibrium. The metastability of the supercooled liquid phase requires the presence of a significant free energy barrier, \( \Delta G_{l\rightarrow c}^* \), located at some intermediate transition state, \( \langle X \rangle_{\text{transition}} = X^* \), which effectively separates the landscape sub-domains of “Amorphous” and “Crystalline” inherent structures, thereby inhibiting the free transitioning of the system to the lower free energy crystalline phase. Recalling that the probability, \( P \), of sampling a microstate corresponding to the macrostate, \( X^* \), is directly related to the system free energy:

\[ P(X^*) \sim \exp \left\{ - \frac{H(X^*) - TS(X^*)}{k_b T} \right\} = \exp \left\{ - \frac{G(X^*)}{k_b T} \right\} \]  

the free energy barrier \( \Delta G_{l\rightarrow c}^* \) can be understood to quantify the relative statistical improbability of sampling “entrance pathways” (generalized transition states) leading to the crystalline phase, which itself can be expressed in terms of the transition state enthalpy, \( H(X^*) \), and entropy, \( S(X^*) \):

\[ H(X^*) = < E + PV >_{X=X^*} \]  

\[ S(X^*) = k_B \ln N(\bar{N}, \bar{E}, \bar{V}|X^*) \]  

where \( N(\bar{N}, \bar{E}, \bar{V}|X^*) \) is the total number of distinct states within some narrow particle number, energy, and volume band about the barrier state \( X^* \). Physically, the large free energy barrier to crystallization is reflective of the statistical rarity of the initial nucleation event corresponding to the formation of a small localized cluster of ordered atoms. Cluster stability is ensured beyond some critical nuclei size, with crystal growth subsequently seen to occur spontaneously.
2.5.1 Nucleation Kinetics

Viewed from a local equilibrium fluctuations based perspective, nucleation kinetics can be understood to depend on three main factors: 1) the probability of randomly sampling a critically sized cluster of atoms of appropriate structure and composition (which initially may even deviate from that of the bulk crystallizing phase) in the parent (metastable) liquid, 2) the kinetics of elementary ordering and chemical attachment processes at the interface, and 3) diffusive transport rates and the relative availability/concentrations of chemical species at the interface required for initial growth and stabilization. In the situation that the composition of the nucleating crystalline phase deviates significantly from that of the parent liquid phase (for instance in the non-polymorphic crystallization of a distant intermetallic), the nucleation process is generally time-dependent and highly complex in nature, with kinetics depending on the relative competition between all three factors. The combined influence of lower critical cluster sampling probabilities associated with the significant compositional mismatch, in addition to lower availabilities of chemical species at the interface and the requirement for larger length-scale diffusive transport from the bulk parent liquid result in significant barriers for nucleation and subsequent growth. Without the absence of any limiting assumptions on the nucleation process, a general analytic description of nucleation kinetics in such situations is currently unavailable. Taking the simplified approach of the Coupled-Flux Model (CFM) [23], however, such cases can be numerically modelled by considering the time-dependent fluxes of chemical species between three generalized regions: namely, the cluster, the immediate region around the cluster (describing some chemically depleted zone in the neighbourhood of the interface), and the parent liquid phase (which subsequently surrounds the shell).

In the case of interface controlled kinetics (i.e. in polymorphic crystallization processes where the liquid and crystal phase possess identical compositions, or when chemical diffusion rates are significantly higher than surface attachment rates), the steady state homogeneous nucleation rate \( I_{ss} \) is predicted under Classical Nucleation Theory (CNT) to be of the form [21][22]:

\[
I_{ss}(T) = A(T) e^{\frac{\Delta G^\ast(T)}{k_B T}}
\]  

\[
\rightarrow N_{nuclei}(t) \approx \int_0^t I_{ss} \cdot V_{liquid} \, dt
\]
where $\Delta G^\ast (T)$ is the Gibbs free energy barrier for nucleation, and $A(T)$ is a temperature dependent kinetic pre-factor. The explicit functional dependencies of these two factors can be understood by first considering that the nucleating cluster size probability distribution, $P(n)$, is directly related to the minimum reversible work of cluster formation, $\Delta G(n)$, in the metastable equilibrium supercooled liquid (essentially by choosing crystalline cluster size $n$ as an order parameter) [21]:

$$\Delta G(n) = G(n) - n\mu_l$$  \hfill (2.17)

where $\mu_l$ is the parent liquid partial molar Gibbs free energy. The equilibrium concentration of ordered clusters of size $n$, $C(n)$, in the liquid is therefore expected to be given by:

$$P(n) \propto e^{-\frac{\Delta G(n)}{k_BT}} \rightarrow C(n) = C_1 e^{-\frac{\Delta G(n)}{k_BT}}$$  \hfill (2.18)

where $C_1 \approx 1$ is the fraction of atomic sites available for cluster growth and is effectively taken to be every atomic site in the system (assuming thermal equilibrium for monomers in the liquid where $P(1) \gg \sum_{n>1} P(n)$ for $n < n^\ast$) [22]. The approximation of a sharp interfacial boundary separating the ordered (spherical) crystalline nuclei and the surrounding disordered liquid phase allows the simplified expression of $\Delta G(n)$ as the combined interaction of two independent terms: 1) a positive surface area dependent destabilizing contribution (proportional to the total nuclei surface area, $4\pi r_n^2$, or equivalently to $(36\pi)^{1/3} \bar{v}^{2/3} n^{2/3}$ where $\bar{v}$ is the specific volume) associated with energetic and entropic penalties linked to the creation of an interface, and 2) a negative volume dependent stabilizing contribution (proportional to the total nuclei volume, $\frac{4}{3} \pi r_n^3$, or to the total number of atoms $n$ in the nuclei) associated with the lower free energy of the bulk crystalizing phase. Denoting the partial molar enthalpy and entropy difference between the liquid and crystalline phase, $\Delta h_{l,c}$ and $\Delta s_{l,c}$ the partial-molar free energy difference driving crystallization is subsequently given by:

$$\Delta \mu_{l,c} = \Delta h_{l,c} - T\Delta s_{l,c}$$  \hfill (2.19)

Denoting, $\sigma_{l,c}$, the liquid-crystal interfacial free energy, $\Delta G(n)$ is simply expressed as [23]:

$$\Delta G(n) = n\Delta \mu_{l,c} + (36\pi)^{1/3} \bar{v}^{2/3} n^{2/3} \sigma_{l,c}$$  \hfill (2.20)
The competition between these two factors results in a free energy maximum at critical nuclei size, \( n^* \), which in conjunction with the associated free energy barrier, \( \Delta G^* = \Delta G(n^*) \), can be determined by maximizing \( \Delta G(n) \) with respect to \( n \), resulting in:

\[
n^* = \frac{32 \pi \bar{v}^2}{3} \frac{\sigma_{Lc}^3}{|\Delta \mu_{Lc}|^3}
\]

\[
\Delta G(n^*) = \frac{16 \pi \bar{v}^2}{3} \frac{\sigma_{Lc}^5}{|\Delta \mu_{Lc}|^2}
\]

From (2.22), the nucleation free energy barrier \( \Delta G^*(T) \) under CNT is seen to be proportional to the liquid-crystal interfacial free energy to the third power, and inversely proportional to the liquid-crystal free energy difference to the second power. Considering the thermodynamic coexistence of the liquid and crystalline phases at the melting point:

\[
\Delta \mu_{Ls}(T_m) = 0 \quad \rightarrow \quad \Delta h_{Ls}(T_m) = T \Delta s_{Ls}(T_m)
\]

translating to a divergence in the nucleation barrier on approach to \( T_m \) from below. The homogeneous nucleation rate near \( T_m \) is subsequently seen to be insurmountably slow in the minimally undercooled domain (reflective of the metastability of the supercooled liquid phase). As temperature is decreased further, however, the increased relative stability of the crystalline phase results in a continuous reduction in the nucleation barrier, translating to increased nucleation rates. In practice, the crystallization enthalpy and entropy are approximately constant near \( T_m \), resulting in a general linear temperature dependence of the chemical potential difference and inverse-squared dependence of the free energy barrier on the extent of undercooling, \( \Delta T = T_m - T \) (or alternatively in terms of the reduced temperature \( \frac{T}{T_m} \)).

\[
\Delta \mu_{Lc}(T) = \Delta h_{Ls}(T) - T \Delta s_{Ls}(T) \approx \Delta h_m \left( 1 - \frac{T}{T_m} \right) = \frac{\Delta h_m}{T_m} \frac{T_m}{T_m} \Delta T
\]

With the equilibrium cluster distribution and concentrations of critically sized nuclei being controlled by the free energy barrier, the kinetic pre-factor, \( A(T) \), can be understood to relate to dynamical aspects of subsequent growth and success rates for super-critical nuclei.
formation[21][22][23]. Under the ballistic steady-state approximation (where only the forward reaction-rates need to be considered), the kinetic pre-factor is given by:

$$A(T) = \rho \beta^*(T) Z_f(T)$$

(2.25)

Where $\rho$ is the liquid density, $\beta^*$ is the growth-rate for critically-sized clusters, and $Z_f$ is the Zeldovich factor, which is related to the curvature of the free energy profile at the top of the free energy barrier:

$$Z_f(T) = \left( \frac{1}{2\pi k_B T} \frac{\partial^2 \Delta G}{\partial n^2} \right)_{n^*}^{1/2} = \left( \frac{\Delta \mu_{ls}}{6\pi k_B T n^*} \right)^{1/2}$$

(2.26)

The Zeldovich factor (often on the order of $0.01 \ll Z \ll 0.1$ [48]) corrects for the relative depletion of larger sized clusters at steady-state, as well as the fact that not all clusters of critical size will successfully proceed to become larger (stable) crystallites, with some stagnating near critical sizes and others re-dissolving under standard thermodynamic fluctuations. The relative flatness of the free energy profile near the top of the barrier (which to second order is controlled by $\frac{\partial^2 \Delta G}{\partial n^2} |_{n^*}$) effectively translates to cluster sizes fluctuating with jump frequency, $\beta^*$, according to a Brownian random walk [24] within a size interval, $\Delta n$, of the critical size where free energy differences are within $\sim k_B T$ from the maximum. With these corrections made through the inclusion of the Zeldovich factor, the only parameter remaining is the growth-rate of critically-sized nuclei, $\beta^*(T)$.

In the case of interface-controlled crystal growth for which growth is not rate-limited by the long-range diffusion of chemical species to the interface, the surface attachment ($r_a$) and detachment ($r_d$) rates associated with the bimolecular monomer addition/subtraction (or attachment/detachment) reactions can be generally expressed under the framework of transition state theory. The attachment or detachment of a single monomer from the crystal surface can be viewed to require the bypass of some elementary activation barrier $\delta g^*$ associated with some intermediate configurational transition state. Defining $\nu$ as the elementary attempt frequency (which is on the order of the mean atomic vibrational frequency), the forward molecular attachment rate $r_a$ can subsequently be expressed as [24]:

$$r_a = \nu \sigma^2 \exp\left(\frac{-\Delta G_{ad}}{k_B T}\right)$$

(2.27)
\[ r_a = v e^{-\frac{\delta g^*}{k_B T}} \]  

Considering only the forward molecular attachment rates (with corrections included in the Zeldovich factor), and factoring in that approximately \( 4n^{*2/3} \) available attachment sites exist at the surface of the spherical nuclei [24], the growth-rate \( \beta^* \) for critically sized nuclei is given by:

\[ \beta^*(T) = 4n^{*2/3}v e^{-\delta g^*/k_B T} \]  

However, with each elementary monomer addition step corresponding to the thermally activated “hopping” of an atom across a distance \( a_0 \) approximately equal to the atomic spacing, \( \beta^*(T) \) is more commonly expressed in terms of the atomic diffusivity:

\[ \frac{6D(T)}{a_0^2} \approx v e^{-\frac{\delta g^*}{k_B T}} \quad \rightarrow \quad \beta^*(T) = \frac{24D(T)n^{*2/3}}{a_0^2} \]  

Thus, in conjunction with the initial rise in the steady-state homogeneous nucleation rate expected due to the decreasing tendency of the free energy barrier with undercooling, a later decay of the nucleation rate is further predicted at extended degrees of undercooling due to the dramatic slowdown of atomic mobilities in the lower temperature domain.

2.5.2 Growth Kinetics

Once a sufficient quantity (which may be as few as one) of supercritical sized clusters have nucleated in the bulk liquid, crystallization kinetics is primarily dictated by the subsequent growth-rates of existing nuclei. The time and temperature dependence of growth-velocities, \( Y_t(T) \), is highly dependent upon whether the underlying process is inherently diffusion (short-range or long-range) or interface limited [24]. In the case of long-range diffusion controlled growth processes, significant compositional mismatch between the liquid and crystallizing phase can be understood to result in the development of a “depletion zone” surrounding the crystal nucleus for which concentrations of required chemical species are significantly depleted relative to the bulk liquid [24]. With each successive layer of crystal growth resulting in a proportional increase in the width of the depletion zone (\( \Delta x \)), and growth-rates being limited by the time required for chemical diffusion from the bulk to the interface, crystal growth-rates are observed to follow:
Crystal growth-rates in long-range diffusion limited systems are subsequently seen to be severely stunted in accord to an inverse-square-root time dependence, and with the inclusion of a constant pre-factor, $k_{ci}(T)$, the (planar) growth-rate generally follows:

$$Y_{t}(T) = k_{ci} \sqrt{\frac{D(T)}{t}} \left(2.31\right)$$

$$\rightarrow r_{nuclei}(t) \approx \int_{0}^{t} Y_{t} \, dt = \frac{k_{ci}}{2} \sqrt{D t}$$

With the exception of long-range diffusion controlled processes described above, crystal growth is well described under a single (time-independent) steady-state growth-velocity, $Y^{ss}(T)$. In specific, the steady-state isothermal (planer) growth-velocity expected under interfacial-control is generally given by [24]:

$$Y^{ss}(T) = \frac{f D(T)}{a_{0}} \left[1 - e^{-\frac{\Delta \mu_{li}(T)}{k_B T}}\right] \left(2.32\right)$$

$$\rightarrow r_{nuclei}(t) \approx \int_{0}^{t} Y^{ss} \, dt = Y^{ss} t$$

where $0 < f < 1$ is the fraction of available sites for attachment, and is generally dependent upon the surface structure and surface-reaction mechanism. Viewing equation 2.18 above, the isothermal (steady-state) growth-velocity is seen to possess a similar temperature profile as the nucleation rate, with rates being zero at the limits of low and high degrees of undercooling. In contrast, however, the exponential dependence of steady-state growth-rate on the liquid-crystal free energy difference results in a much more rapidly increasing linear temperature dependency in the minimally undercooled domain.
2.5.3 Critical Cooling Rate

From a theoretical standpoint, thermodynamic forces driving crystallization can be inhibited in any alloy system should the cooling rate be sufficiently high. Imposing a cutoff crystalline fraction (often determined by standard detection limits of $10^{-6}$ or 0.0001 percent crystalline), the associated critical cooling rate $R_c$ is a natural metric for glass forming ability. As discussed in the previous sections, the dependencies of the critical cooling rate can be separated into two main factors: 1) the rate or frequency at which new crystalline nuclei spontaneously form in the metastable equilibrium liquid, $I_c(T)$, and 2) the growth-rate or growth-velocity of existing crystal nuclei, $Y(T)$. Taking the simplifying assumption of a steady-state nucleation and growth process, with isothermal nucleation rate per unit volume of liquid, $I^{ss}(T)$, and steady-state isothermal growth-velocity, $Y^{ss}(T)$, the expected crystal volume fraction, $X_{\text{crystal}}(t)$, can be approximated in the initial stages of crystallization where crystal volume fractions are minimal, i.e. for small time, $t$, when:

$$X_{\text{crystal}} = \frac{V_{\text{crystal}}}{V} \approx \frac{V_{\text{crystal}}}{V_{\text{liquid}}} \approx 0$$  \hspace{1cm} (2.33)

First, considering that the radius of a single nuclei, $r_{\text{nuclei}}(t)$, after time $t$ of nucleating is approximately equal to $Y^{ss} * t$, the corresponding volume of the single spherical crystallite is given by:

$$V_{\text{nuclei}}(t) = \frac{4}{3} \pi r^3(t) \approx \frac{4}{3} \pi (Y^{ss} t)^3 = \frac{4}{3} \pi Y^{ss} t^3$$  \hspace{1cm} (2.34)

Using this expression, the total crystallized volume after time $t$ can be estimated by integrating over the volumes of all individual crystals nucleated since time $t = 0$.

$$V_{\text{crystal}}(t) \approx \int_0^t I^{ss}(t') * V_{\text{liquid}}(t') * V_{\text{nuclei}}(t-t') \, dt'$$  \hspace{1cm} (2.35)

In the steady state approximation, $I^{ss}$ and $V_{\text{liquid}} \approx V$ are effectively time independent, therefore:
\[ X_{\text{crystal}}(t) = \frac{V_{\text{crystal}}(t)}{V} \approx 1^{ss} \int_0^t \frac{4\pi}{3} Y^{ss^3}(t - t')^3 \, dt' = \frac{\pi}{3} I^{ss} Y^{ss}^3 t^4 \] (2.36)

With this in mind, the time required for crystallization up to cutoff crystalline fraction \( x \) (which may for example be imposed by instrumental detection limits) under isothermal conditions at temperature \( T \), \( t_{x}^{ss}(T) \) is:

\[ t_{x}^{ss}(T) = \left( \frac{3x}{\pi I^{ss}(T) Y^{ss}(T)^3} \right)^{\frac{1}{3}} \] (2.37)

The isothermal crystallization rate can therefore be seen to be controlled by the weighted product of the nucleation rate and growth-velocity. With the free energy barrier diverging to infinity in the minimally undercooled domain and gradually decreasing upon extended undercooling, the nucleation rate is generally observed to peak at significantly higher extents of undercooling relative to the growth-velocity. These considerations, in conjunction with the higher weighting of the growth-velocity (by a power of 3) on the isothermal crystallization rate, are seen to result in peak isothermal crystallization rates in the high temperature supercooled domain. This is most evident upon analysis of Time-Temperature-Transformation (T-T-T) diagrams of common glass forming alloys, for which the nose temperature (determined by the tangent intersection of the linear cooling rate curve starting at \( T_m \) with the T-T-T curve is often found to lie near:

\[ T_{\text{nose}} \approx 0.9T_m \] (2.38)

While the quenching process involved in glass formation is inherently non-isothermal, the slope (dT/dt) of the tangent linear cooling curve intersecting at the nose temperature is often a good upper-bound/conservative estimate of the critical cooling rate, \( R_c(x) \).

### 2.6 Predictive Indicators of Glass Forming Ability

Due to the complex functional dependencies of glass forming ability on a host of thermal history dependent and compositionally sensitive parameters, in conjunction with the vast compositional spaces inherent to multicomponent BMG systems, predictive optimization methods for the identification of new high GFA alloys possess severe limitations in practicality and scope. Lately, significant effort has been placed on the identification of simple and easily extractable
(either through modeling, simulation, or experiment) parameters that strongly correlate with high glass forming ability in general, with the greater goal of using said parameters for predictive compositional tuning purposes.

In line with these notions, heuristic guidelines first introduced by Inoue [25] identify three key features of the stabilized supercooled phase: 1) multicomponent systems, with a generally monotonic improvement in stability as number of components is increased, 2) presence of significant atomic size ratios greater than 12 percent, and 3) large negative heats of mixing. Based on considerations of local topological stability of short-range packing structures in multicomponent mixtures, Egami [26] added two additional conditions favorable for bulk metallic glass formation in higher order ternary and quaternary systems: 4) increased interaction between small and large elemental components, and 5) decreased interaction and/or repulsive interactions between smaller elemental components. Combined, these guidelines serve to illustrate the complex interplay between compositional ordering, short-range topological stability and interactions, and global phase stability of the melt. In the absence of explicit relationships outlining the interdependencies of these different factors and their connections to GFA, it has proven difficult to translate these heuristic guidelines into useful GFA predictors.

While empirical in nature and requiring more detailed knowledge of the physical system in question, thermos-physical properties such as the reduced glass transition temperature $T_{rg}$, the temperature difference between glass transition and onset crystallization (from below), $\Delta T_x$, the gamma value, $\gamma$, and the viscous fragility parameter, $m$, are found to correlate well with glass forming ability in general.

\[
T_{rg} = \frac{T_g}{T_l}
\]  
\[
\Delta T_x = T_x - T_g
\]  
\[
\gamma = \frac{T_x}{(T_g - T_l)}
\]  
\[
m = \left(\frac{\partial\log_{10}\eta(T)}{\partial(T_g/T)}\right)_{T=T_g}
\]
The reduced glass transition temperature can be understood to quantify the extent of undercooling required for glass formation in a normalized fashion, with larger values expected for higher GFA alloys near deep eutectics. $\Delta T_x$ is reflective of devitrivication kinetics and crystallization rates in the highly undercooled liquid, a largely diffusion controlled domain. The liquid fragility parameter further serves to differentiate “strong” and “fragile” glasses based on how abrupt the viscous slowdown process is on approach to the glass transition temperature, with lower fragilities being generally indicative of lower atomic mobilities in the supercooled domain and high GFA. Each of these parameters serve to quantify key influencing factors governing crystallization kinetics in general, the thermodynamic forces driving crystallization, and the kinetic factors inhibiting nucleation and growth.

2.6.1 Interface Stability and the Liquid-Crystal Interfacial Free Energy

Due to the interfacial free energies’ influence on the nucleation barrier and role in dictating nucleation kinetics, significant effort has been placed on the investigation of its key influencing factors and prediction. Turnbull [27] revealed the strong correlation between the gram-atomic (molar) interfacial free energy, $\sigma_{i,s}^M$, and the latent heat of fusion, $\Delta h_{s,l} = \Delta s_{s,l}/T_m$, for a range of elemental metals:

$$\sigma_{i,s}^M = \sigma_{1,s} \rho^{-2/3} N_A = \alpha \Delta h_{s,l} = \frac{\Delta s_{s,l}}{T_m}$$

(2.42)

where $\rho^{-2/3}$ is the density of atoms on the crystal interface, $N_A$ is Avogadro’s number, and $\alpha$ is the Turnbull coefficient which is dependent upon the structure and orientation of the crystal at the interface, ranging between 0.45 for closely packed structures (e.g. fcc or hcp), and 0.33 for more open structures (such as the diamond cubic). Correlations to the latent entropy of fusion suggest an intrinsic connection between the interfacial free energy and the extent of configurational mismatch between the liquid and crystal phase. Recent experimental determinations of Turnbull coefficients [28] and liquid-crystal interfacial energies in the Cu-Zr system were highly successful in predicting trends in critical casting diameters, further enforcing the importance of interfacial properties and the general controlling nature of the nucleation barrier on glass forming ability. Unfortunately, without exact knowledge of the structure and associated optimal crystal cluster geometries and orientations at the liquid-crystal interface, the direct simulation and calculation of interfacial free energies over a broad range of compositions.
in multicomponent alloy systems is largely unfeasible. Surprisingly, however, molecular dynamics investigations conducted by Kang et al. [28] of glass-glass interfacial energies were similarly successful in predicting trends in critical casting diameters in the Cu-Zr system (over the 30-54 percent copper compositional range). Simulation methods involved cutting and separating the supercooled liquids along an arbitrary plane, relaxing the structures, and calculating the difference in system energies after the recombination of the two separate faces. Considering the observed predictive success of this method while completely neglecting to consider crystalline phase properties, these findings further suggest that glass forming ability, and interfacial properties in general, are strongly controlled by the short-range chemi-topological ordering and bonding properties of the disordered liquid phase.

2.6.2 Liquid and Amorphous Phase Packing Efficiency

Amorphous phase packing efficiency and the extent of free volume in the liquid melt has been identified to be one of the best single indicators of glass forming ability. In accordance with these notions, amorphous phase densities have been observed to strongly correlate with underlying compositional dependencies of glass forming ability in the Cu-Zr system over a broad compositional range [29]. Li et al.’s investigation of compositional dependencies of fractional density changes (or excess free volume) upon crystallization showed direct correspondence with critical casting thicknesses, with experimental results indicating minimal density changes (minimal free volumes) for high GFA compositions of Cu$_{64}$Zr$_{36}$, Cu$_{56}$Zr$_{44}$, and Cu$_{50}$Zr$_{50}$. Considering correlations between liquid free-volume, viscosities at the liquidus/melting temperature [11], and the kinetic fragility parameter [30], these results suggest that enhanced atomic mobility constraints associated with more efficient liquid-state atomic packing in these select compositions are the root of their higher glass forming ability. Further consistent with these notions is the general success of the Miracle Glass model in predicting high glass forming compositions based on simple considerations of ideal atomic-size ratios for the attainment of optimal short-range cluster packing efficiencies[9][10].

2.6.3 Icosahedral Short-range Ordering

Owing to their greater topological and energetic stability as isolated units, as well as their respective 12-point group symmetry which is generally incompatibility with translationally symmetric structures, icosahedral ordering has been argued to play a critical role in the
stabilization of supercooled melts [31][32]. Recent findings have shown a general exponential dependence of structural relaxation times with the medium-range connectivity of icosahedral clusters in the Copper-Zirconium metallic liquids [32], linking the formation of large-scale icosahedral networks with slower liquid state dynamics. In addition to the general influence of icosahedral ordering on slowing atomic transport properties, topological aspects regarding icosahedral structures are arguably just as (if not more) important. Despite the inability to form translationally periodic structures, the icosahedral coordination is topologically close-packed (containing only tetrahedral interstices). Moreover, icosahedral packing of distorted polyhedra produces highly globally efficient packing structures [33]. With the interfacial free energy being strongly related to the extent of short-range structural similarity between the liquid and crystal boundary, and based on the general chemical and topological short-range incompatibility of the icosahedra with that of common crystalline and near crystalline states, one would expect high fractions of icosahedral clusters to inhibit crystallization kinetics. In cases where low free energy crystalline polymorphs exist with compatible symmetries and structures, however, high degrees of icosahedral short-range ordering may have the destabilizing effect of lowering the interfacial free energy. Such an example is evident in the primary nucleation of the metastable quasi-crystalline Icosahedral (-i) phase in Zr$_{59}$Ti$_3$Cu$_{20}$Ni$_{8}$Al$_1$, where nucleation measurements indicated interfacial free energies of $\sigma_{lc} = 0.01 \pm 0.004$Jm$^{-2}$ [31], a remarkably low value relative to other crystalline phases. Nonetheless, in complex multicomponent systems where crystallization is often diffusion limited, decreased melt free volume and higher melt viscosities attributed to increased icosahedral short-range ordering has been found to largely outweigh associated destabilizing effects on interfacial free energies [33].

2.6.4 Compositional Short-Range Ordering and Complexity

The general enhancement of supercooled melt stability observed in BMGs under increasing number of components, as well as the emphasis on the presence of significant atomic size ratios (>12%) between constituent alloy elements can be understood to reflect the intricate connection between GFA and the degree/complexity of chemical short-range ordering in the disordered phase. With the likelihood of the primary nucleating crystalline phase possessing identical bulk compositions to that of the parent melt becoming increasingly low as the number of components increase, and with greater atomic size-mismatch between constituent elements reducing the stability of less compositionally constrained solid solution phases while simultaneously allowing
for more efficient packing in the disordered phase through enhanced preferential ordering of chemical species and the filling of interstitial sites, crystal nucleation and growth kinetics can subsequently be seen to become heavily (short and long-range) diffusion-limited processes. The increased compositional complexity that is likely to exist in the crystallizing phase further inhibits crystallization kinetics due to the requirement for longer length-scale chemical transport and rarer structural reordering events for the initial nucleation and subsequent growth to occur. Dynamic decoupling associated with the broad range of atomic mobilities expected among larger and smaller chemical species adds further constraints on crystallization rates, with diffusion limitations primarily being controlled by the slowest, least mobile components.
Chapter 3

3 Methodology and Computational Details

3.1 Molecular Dynamics

Many body molecular dynamics (MD) simulations conducted in this work for the investigation of structural, bonding, and kinetic property evolution in the liquid and glassy domains were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [34]. In particular, atomic interactions for the binary alloys simulated in this study are described using empirically derived Embedded Atom Method (EAM) interatomic potentials. In the EAM model, the total system potential energy, $V_{tot}$, is expressed by the following expression [35]:

$$
V_{tot} = \frac{1}{2} \sum_{i \neq j} \varphi_{s_i \sigma_j}(r_{ij}) + \sum_i F_{s_i}(\bar{\rho}_i)
$$

(3.1)

The first term in this expression is the sum of all pair interactions between atoms in the system, where $\varphi_{s_i \sigma_j}(r_{ij})$ is the pair-interaction potential between atom i of chemical-type $s_i$, and atom j of chemical-type $s_j$, as a function of their spatial separation $r_{ij}$. Many-body contributions to atomic interactions are accounted for in the second term of this expression involving sums over individual atom embedding energies, $F_{s_i}$, which itself is dependent upon the mean local electron density experienced by host atom i, $\bar{\rho}_i$, as induced by all other atoms in the system. The mean local electron density as experienced by host atom i is subsequently given as a sum over individual atom electron density functions, $\rho_{s_j}(r_{ij})$, as:

$$
\bar{\rho}_i = \sum_{i \neq j} \rho_{s_j}(r_{ij})
$$

(3.2)

Simulations of atomic trajectories under the NVE microcanonical ensemble can subsequently be understood to follow from discrete numerical time integration of the classical (Hamiltonian) evolution equations, with atomic forces, $F_i$, directly calculated through the evaluation of the three-dimensional potential energy gradient with respect to atomic positions, $r_i$: 
Assigning initial atomic coordinates, \( r_i(0) \), according to some known crystal structure or phase, velocities, \( v_i(0) = p_i(0)/m_i \), are initialized by appropriate sampling (ensuring that net system momentum is zero) of the Maxwell-Boltzmann distribution:

\[
f(v) = \left( \frac{m}{2\pi k_B T} \right)^{1/2} e^{-mv^2/2k_B T}
\] (3.4)

With initial atomic coordinates and momenta configured, subsequent time evolution of atomic coordinates and velocity/momenta under discrete time-step, \( \Delta t \) (on the order of 1fs), following the iterative NVE velocity Verlet time-integration algorithm used in this work is expressed through the simple three-step procedure:

1) \( p_i \rightarrow p_i + \frac{\Delta t}{2} F_i \)

2) \( r_i \rightarrow r_i + \Delta t \frac{p_i}{m_i} \)

Recalculate Forces

3) \( p_i \rightarrow p_i + \frac{\Delta t}{2} F_i \)

System temperature and pressure control for use in more generalized NVT or NPT operating conditions are conducted through modified evolution equations ensuring correct statistical ensemble properties. In this work, standard Nose-Hoover temperature thermostats and pressure barostats were used.
3.2 Model Generation

![Visual overview of the simulated melt and quench process used for metallic glass model generation](image)

**Figure 3.1:** Visual overview of the simulated melt and quench process used for metallic glass model generation

Bulk liquid and glassy phases were generated by a simulated melting and quenching process (as depicted in Figure 3.1). Initial configurations comprised of 6000-8000 atom systems of desired compositions, randomly ordered according to an arbitrary crystal lattice. Following an initial enthalpy minimization stage, systems were rapidly heated from 300K to 2100-2300K over a duration of ~1000ps, and subsequently relaxed for ~2500ps under isothermal-isobaric conditions. With internal structural relaxation times of liquid alloys being on the order of picoseconds in this high temperature regime, this procedure provides sufficient time for the equilibration of the high temperature liquid melt. Additional information on the model generation, validation, and reproducibility are included in Appendix C. Viewing Figure 3.2 below, this is further evidenced by the general stationarity and stability of standard thermodynamic observables extracted immediately after relaxation. Following equilibration, systems were subsequently cooled down to a temperature of 50K through a series of 25K quench (~100ps) and hold(~150ps) stages, corresponding to an average linear cooling rate of ~0.1K/ps. Under parallel computation using 64 nodes (IBM iDataPlex DX360M2) with a total of 512 cores (Intel Xeon E5540) at 2.53GHz, with 16GB RAM per node (2GB per core), total computational time required for the simulated quenching process ranged from 16-24hrs (constituting the main limitation preventing lower cooling rate quenching). Throughout the quenching process, zero pressure isobaric conditions were applied using NPT Nose-Hoover temperature and pressure controls under 1fs integration.
time-steps. Further property analysis at relevant temperatures of interest was conducted following additional 300ps NPT/NVT/NVE relaxation runs.

![Stability of Melt Properties After Relaxation](image)

**Figure 3.2:** Demonstration of the stability and stationarity of thermodynamic properties in the high temperature Cu$_{50}$Zr$_{50}$ liquid melt after equilibration

### 3.3 Calculation of Thermodynamic and Bulk Physical Properties

Thermodynamic properties (entropies, free energies) were obtained using the 2PT method of Lin, Blanco, and Goddard [36][37]. The method allows for the accurate calculation of thermodynamic properties in complex multicomponent systems, requiring short MD simulations of (32ps used in this study) for the extraction of the atomic vibrational density of states through the Fourier transform of atomic velocity autocorrelation functions. System thermodynamic contributions are separated into two components; a harmonically vibrating solid phase, and a diffusive hard sphere phase accounting for inherent anharmonicities. The method hinges upon the appropriate decomposition of the vibrational density of states (DOS) for each component in the mixture into a diffusive gas-like contribution, $S_g(\nu)$, and a harmonically vibrating solid component, $S^s(\nu)$. Once the phase contributions are decomposed, analytic relationships for the thermodynamic
properties of the quantum harmonic solid, and the diffusive hard-sphere mixture (based on Enskog theory) are utilized for the calculation of total system properties (See references [36] and [37] for a more detailed description of the 2PT methodology).

In cases where the primary crystalline phase is known a priori, melting points ($T_m$) of respective systems were estimated based on the phase equilibrium condition of equal Gibbs Free Energy for liquid and crystal phases. Following the work of Zhang, An, and Goddard, $\Delta \mu (T_g)$ is utilized in this work as a common metric for evaluating phase stabilities of respective amorphous/supercooled phases, with glass transition temperatures ($T_g$) estimated by the common intersection point of polynomial fits to low temperature and high temperature enthalpy data (see Zhang et al. [38], 2011, and Mendelev et al., 2009 [39]).

Second order thermodynamic properties (constant volume/pressure heat capacities and thermal expansion coefficient) were calculated through two different methods: direct calculation of enthalpy/energy and volume temperature derivatives through symmetric finite differencing of cooling curve data, and secondly, through the fluctuations approach as expressed in the following relations:

\[
C_p \equiv \frac{\partial H}{\partial T}_P = \frac{1}{k_B T^2} < \delta H^2 >_{NPT}
\]

\[
C_v \equiv \frac{\partial U}{\partial T}_V = \frac{1}{k_B T^2} < \delta U^2 >_{NVT}
\]

\[
\alpha_T \equiv \frac{\partial V}{\partial T}_P = \frac{1}{k_B T^2} < \delta V^2 >_{NPT}
\]

Similarly, the fluctuations approach was utilized for the calculation of isothermal compressibility, $\beta_T$ (or inverse bulk moduli, $B_T$):

\[
\beta_T = B_T^{-1} = -\frac{1}{V} \frac{\partial V}{\partial T}_T = \frac{1}{k_B T} < \delta V^2 >_{NPT}
\]

Utilizing these results, (pseudo) Gruneisen parameters were extracted through the following relation:
While the two calculation methods yielded consistent results, values obtained through the fluctuation method were found to generally exhibit more noise. Subsequently, for the calculation of (pseudo) Gruneisen parameters, heat capacities and thermal expansion coefficients corresponding to those directly obtained from cooling curve data were used.

### 3.4 Calculation of Transport Properties and Fragility

Equilibrium Green-Kubo methods were used for the calculation of atomic diffusivities and shear viscosities in both systems under study. Under the Green-Kubo formalism, atomic diffusivities are directly related to the velocity autocorrelation function through the following relation:

\[
D = \frac{1}{3} \int_0^\infty \langle v(t + t') \cdot v(t) \rangle \, dt'
\]  

(3.11)

Denoting the velocity power spectral density as \( P(v) \), the diffusion coefficient can be equivalently expressed in terms of the zero frequency power spectral density:

\[
P(0) = \int_{-\infty}^{\infty} \langle v(t + t') \cdot v(t) \rangle \, e^{-2i\pi(0)} \, dt' = 2 \int_0^\infty \langle v(t + t') \cdot v(t) \rangle \, dt' = 2D
\]  

(3.12)

\[\Rightarrow D = P(0)/2\]

An initial 300ps relaxation run, followed by a 32ps velocity sampling run under NVT conditions was found to be sufficient for proper convergence of diffusivities.

Similarly, viscosities are directly related to the stress autocorrelation functions \( \langle P_{\alpha\beta}(t)P_{\alpha\beta}(0) \rangle \) through the following relation:

\[
\eta = \frac{V}{kT} \int_0^\infty \sum_{\alpha\beta} \langle P_{\alpha\beta}(t)P_{\alpha\beta}(0) \rangle \, dt
\]  

(3.13)

where \( P_{\alpha\beta} \) is the symmetrized traceless portion of the stress tensor \( \sigma_{\alpha\beta} \), defined as:
\[ \sigma_{\alpha\beta} = \frac{1}{V} \sum \left[ \frac{p_{i,\alpha} p_{i,\beta}}{m_i} + (r_{i,\alpha})(F_{i,\beta}) \right] \]  
\[ P_{\alpha\beta} = \frac{1}{2} (\sigma_{\alpha\beta} + \sigma_{\beta\alpha}) - \frac{1}{3} \delta_{\alpha\beta} \left( \sum_y \sigma_{yy} \right) \]  

The above formulation averages over the five independent components of the traceless stress tensor \( P_{xy}, P_{yz}, P_{zx}, \frac{1}{2} (P_{xx} - P_{yy}), \text{ and } \frac{1}{2} (P_{yy} - P_{zz}) \) (with the last two being equivalently to the first three by rotational invariance [40]), allowing for improved autocorrelation function statistics. In order to acquire sufficient convergence of stress autocorrelation functions, simulation runs ranged from 1000-3000ps (under 1fs time-steps), ensuring sampling times of at least 50 times underlying relaxation times.

Viewing the initial decay of the \( \text{Cu}_{50}\text{Zr}_{50} \) (900K) stress autocorrelation function plotted below in Figure 3.3, these conditions can be seen to hold well down into the moderately undercooled liquid regime. Estimated relaxation times are seen to be on the order of \( \tau_{\text{shear}} \approx 5\text{ps} \) (5000fs), with total simulation times of 2000ps (2000000fs) corresponding to about 400 \( \tau \) (which is well above the 50X lower bound). Viscosity calculations were however limited to temperatures in the range \( T > T_g + 125K \), largely due to computational limitations and associated convergence issues encountered at lower temperatures (higher viscosities).
Figure 3.3: Initial decay of Cu-Zr 900K stress autocorrelation function

Kinetic fragility (m) and strength parameter (D∗) were extracted through viscosity fitting to the VFT form:

\[ \eta(T) = \eta_0 \exp\left(\frac{D^*T_0}{T - T_0}\right) \] \hspace{1cm} (3.16)

Where \( \eta_0 \) is the high temperature viscosity limit, \( T_0 \) is the divergent temperature (often close in value to the Kauzmann temperature \( T_K \)), and \( D^* \) is the strength parameter, a common fragility metric with larger \( D^* \) indicative of stronger glasses. The above VFT form was fit to viscosity data collected in 25K intervals over a temperature range of \( 1.2 - 1.8T_g \). Once the VFT fit parameters were extracted, the kinetic fragility parameter, \( m \), was also determined through the following relation:

\[ m = \left(\frac{\partial \log_{10} \eta(T)}{\partial (T_g/T)}\right)_{T=T_g} = \frac{T_g \ast D^*T_0}{\log(10)} \frac{1}{(T_g - T_0)^2} \] \hspace{1cm} (3.17)

However, due to the significantly higher cooling rates experienced under the simulated quench, the standard rheological definition for the glass transition temperature based on viscosities equaling \( 10^{12}\) Pa \( \cdot \) s is not appropriate for arriving at consistency with the calorimetric \( T_g \).
extracted from the thermodynamic cooling curve results, nor for obtaining representative estimates of liquid fragilities using the above relation (for which fragilities will be artificially over-valued). In order to partially account for associated cooling rate effects, a rescaling of the rheological condition for the glass transition temperature from $\eta(T_g) = 10^{12}$ Pa $\cdot$ s to $\eta(T_g) = 10^3$ Pa $\cdot$ s was implemented in the present study.

The physical basis for this rescaling can be understood by first considering that the process of glass formation is intrinsically linked to the competition between underlying internal (structural, enthalpic, etc.) relaxation times ($\tau_{\text{int}}$) governing equilibration kinetics, and experimental/observational timescales ($\tau_{\text{obs}}$) acting to limit the extent of relaxation and configurational sampling possible. With experimental timescales being inversely proportional to the cooling rate ($\beta = \frac{dT}{dt}$) at any given temperature and pressure along the quench, system dynamics are seen to be effectively frozen out below temperature $T_g$ where $\tau_{\text{int}}(T_g) \approx \tau_{\text{obs}}$. Considering that viscosities governing bulk shear/structural relaxation are proportionally dependent upon underlying shear relaxation times ($\eta \propto \tau_{\text{shear}}$), this condition is generally satisfied for the majority of liquid melts under standard experimental operating conditions (where $\tau_{\text{obs}} \approx 10^2 - 10^3$ s) when viscosities are on the order of $10^{12}$ Pa $\cdot$ s, hence the standard rheological condition for the glass transition temperature: $\eta(T_g) = 10^{12}$ Pa $\cdot$ s. Based on these fundamental principles underlying the glass transition phenomena in general, one arrives at the following scaling law for viscosities at $T_g$ under simulated cooling rates:

$$\eta(T_g) \propto \tau_{\text{shear}}(T_g) \approx \tau_{\text{obs}} \propto \frac{1}{\beta}$$

$$\Rightarrow \frac{\eta(T_g)|_{\beta_{\text{sim}}}}{\eta(T_g)|_{\beta_{\text{exp}}}} = \frac{\tau_{\text{sim}}}{\tau_{\text{exp}}} = \frac{\beta_{\text{exp}}}{\beta_{\text{sim}}}$$

(3.18)

With $\eta(T_g)|_{\beta_{\text{exp}}} = 10^{12}$ Pa $\cdot$ s corresponding to standard experimental operating conditions where cooling rates are on the order of $\beta_{\text{exp}} \approx 10^2$ K/s, and with simulated cooling rates utilized in this study being $\beta_{\text{sim}} = 10^{11}$ K/s, the previously stated rescaled viscosity condition can be reconciled:
\[ \eta(T_g)_{\beta_{\text{sim}}} = (10^{12} \text{Pa} \cdot \text{s}) \times \frac{(10^2 \text{K/s})}{(10^{11} \text{K/s})} = 10^3 \text{Pa} \cdot \text{s} \]  

(3.19)

In order to differentiate between the calorimetric \( T_g \) estimated from cooling curve data in the remainder of this paper, the rheological glass transition temperature defined by this rescaled viscosity condition will be denoted: \( T_g^{\eta=10^3 \text{Pa} \cdot \text{s}} \).

### 3.5 Calculation of Structural Properties

Partial radial distribution functions (\( g_{\alpha\beta} \)) are calculated through standard binning techniques formally expressed in the following relation:

\[ g_{\alpha\beta}(r) = \frac{V}{N_{\alpha}N_{\beta}} < \sum_{i=1}^{N_{\alpha}} n_{i\beta}(r) \frac{4\pi r^2 \Delta r}{4\pi r^2 \Delta r} > \]  

(3.20)

0.1\( \text{A} \) bin sizes were used (\( \Delta r = 0.1\text{A} \)), and in order to improve statistics, PRDF results were averaged over 5 separate snapshots (taken over a 32\( \text{ps} \) duration).

Short-range ordering and structure is primarily investigated through the analysis of radical Voronoi tessellation results. Voronoi tessellation involves the decomposition of the system into a finite number of polyhedra centered about the various atomic sites, with volumes encompassed by each polyhedra consisting of the set of all points closer to that given atomic center than any other. In standard Voronoi tessellation, polyhedra edges correspond to the intersection of planes positioned at the perpendicular bisector connecting neighbouring atomic centers, with faces corresponding to the common area shared by both atoms. Radical Voronoi tessellation generalizes the above framework to poly-disperse systems by scaling plane positions according to the ratios of atomic radii. Polyhedra types are subsequently differentiated according to their Voronoi indices \(< n_3, n_4, n_5, n_6, \ldots n_{10} >\), where \( n_i \) denotes the number of \( i \)-edged faces possessed by the given Voronoi polyhedron (with \( i \) ranging from 3-10 due to geometrical constraints). As each face corresponds to a “bond” between the central and corresponding atomic neighbour, coordination number (CN) can be determined by summing the total number of faces, or \( \text{CN} = \sum_i n_i \). In this study, radical Voronoi tessellation is conducted through the Voro++
package [41]. System snapshots are taken every 512 time-steps over a sampling duration of 32ps allowing for improved cluster statistics.

Atomic nearest-neighbour information extracted from Voronoi tessellation was further utilized for the investigation of local compositional ordering through calculation of the Warren-Cowley parameter [42]. Denoting $<\text{CN}>$ as the mean total coordination number (or mean number of nearest-nearest neighbours), $<\text{CN}_{ij}>$ the mean coordination of species j atoms about species i central atoms, and $c_i$ the bulk stoichiometric concentration of species i, the Warren-Cowley parameter, $\alpha_p$, is calculated through the following relation:

$$
\alpha_p = \frac{c_i <\text{CN}> - <\text{CN}_{ij}>}{c_i <\text{CN}>} = \frac{c_j <\text{CN}> - <\text{CN}_{ij}>}{c_j <\text{CN}>}
$$

(3.21)

The Warren-Cowley parameter serves to quantify the average deviation of local compositions (comprised of atoms in the first coordination shell) from that of the bulk (stoichiometric composition) in a normalized fashion. Greater local compositional deviations from bulk stoichiometry are a signature of enhanced compositional short-range ordering (CSRO) in the amorphous phase [42].
Chapter 4

4 Investigating the Atomic-Level Influences of Glass Forming Ability in Ni-Al and Cu-Zr Metallic Glasses

Sections of this chapter have been published in “The Journal of Chemical Physics” under the title of “Investigating the atomic level influencing factors of glass forming ability in NiAl and CuZr metallic glasses” [43]. Text and figures have been reproduced with permission from the American Institute of Physics.

4.1 Introduction

The high glass forming ability of zirconium-copper based multicomponent alloys makes the binary Cu-Zr system a prime focal point for analysis. Recently, independent studies investigating the compositional dependencies of glass forming ability in the Cu-Zr system have uncovered a number of influencing factors that inhibit crystal nucleation and growth [28][29]. Li et al.’s [29] investigation of compositional dependencies of percent density changes (or excess free volume) upon crystallization \((\rho_c - \rho_{liq})/\rho_c\) showed a direct correspondence with critical casting thicknesses, with experimental results indicating minimal density changes (minimal free volumes) for high GFA compositions of \(Cu_{64}Zr_{36}\), \(Cu_{56}Zr_{44}\), and \(Cu_{50}Zr_{50}\). In accordance with free-volume theories for diffusive motion [44] and observed correlations between density change upon crystallization and viscosities at the liquidus/melting temperature [11], these results suggest that enhanced atomic mobility constraints associated with more efficient liquid-state atomic packing in these select compositions are the cause of their higher glass forming ability.

Consistent with these notions, Russew et al.’s [30] experimental investigations into compositional dependencies of melt fragility in the Cu-Zr alloy system found a strong correlation between melt fragility and glass forming ability, with findings showing a clear minimum at the high GFA composition \(Cu_{64}Zr_{36}\). On a parallel front, experimentally determined Turnbull coefficients and liquid-crystal interfacial energies, as well as molecular dynamics calculations of glass-glass interfacial energies were similarly successful in predicting trends in critical casting diameters in the Cu-Zr system [28]. With this in mind, Kang et al. proposed a nucleation barrier controlling nature dictating the glass forming ability of Cu-Zr alloys, with results of glass-glass interfacial
energy calculations suggesting an underlying link to compositional and topological short-range ordering [28].

Unlike Cu-Zr, the Ni-Al system has recently been the focus of study due to its anomalously high crystallization rate for an equimolar binary alloy. While both systems possess similar atomic size ratios, similar atomic mobilities throughout the quench regime, and identical primary nucleating crystal phases (B2 phase), the equimolar Ni$_{50}$Al$_{50}$ alloy possesses critical cooling rates orders of magnitude higher than Cu$_{50}$Zr$_{50}$, with crystal nucleation even being accessible under molecular dynamics timescales. Tang and Harowell’s [45] molecular dynamics investigation of Ni$_{50}$Al$_{50}$’s anomalously low unidirectional crystal growth-rates in comparison to Cu$_{50}$Zr$_{50}$ uncovered striking differences in the extent of chemical ordering present at the liquid-crystal interface. Large amplitude and long length-scale density correlations extending well into Ni-Al’s parent liquid phase were observed at the interface, while in contrast, correlations in the Cu-Zr parent phase rapidly decayed away from the boundary, with little indication of induced ordering beyond a few atomic layers [45]. Understanding the underlying factors controlling the susceptibility for ordering at the interface may thus be key to understanding glass forming ability in general. It is likely that the differences observed are linked to more intrinsic differences in the nature of short-range chemical and topological ordering between the two systems.

Recent analysis of glass pair-correlation functions for a number of different alloy systems have identified “hidden” topological differences between poor and ideal glass formers [46]. It was found that scaled peak positions in the pair distribution function of glassy systems can roughly be decomposed into those corresponding to fcc or bcc crystal structures. Higher GFA alloys were found to exhibit a higher degree of intermixing between these corresponding fcc and bcc “hidden orders”, suggesting greater geometric frustration in these alloys inhibited crystallization [46]. While not discussed by Wu et al., a greater extent of topological entanglement of hidden orders and thus medium-range geometric frustration in the Cu-Zr system may be a major constraining force on the degree and length-scales of induced crystalline ordering at the interface.

Furthermore, considering the similar compositional trends observed for interfacial free energies, extent of free volume, compositional/polytetrahedral short-range ordering, and compositional ordering at the interface, it is possible that a connection exists to some more fundamental underlying property at the bonding level. Currently, limited information is available regarding
underlying bonding, short-range ordering, transport, and structural relaxation properties of the Ni-Al and Cu-Zr amorphous phases, largely hindering the ability to concretely investigate such underlying connections.

Despite these significant advances, a clear-cut design approach for the compositional tuning of glass forming ability in BMGs a priori has yet to be identified. Current computational and analytic tuning methods are severely limited in their applicability due to a number of non-trivial factors. Many of the identified GFA indicators and influencing factors (including the majority of those discussed above) are not single phase properties, and often are related to properties of the disordered and crystallizing phases and/or the interface between the two. In complex multi-component systems, the equilibrium crystalline phase is rarely known before hand, with the crystallization pathway leading to the final equilibrium phase more often than not being a multi-step process involving several (also likely unknown) intermediate metastable phases. These considerations would then suggest the potential existence of severe limitations on the practicality of a computational (or experimental) method capable of rapid, accurate, and compositionally robust GFA tuning. Assuming an accurate inter-atomic potential is available, current molecular dynamics simulations methods readily allow for the sampling of liquid, supercooled, and glassy phase (albeit, rapidly quenched) properties over vast compositional spaces with little to no prior knowledge of the underlying systems. In this respect, the identification of GFA indicators and influencing factors relating solely to properties of the amorphous phase is of utmost importance. Many of the proposed GFA tuning methods and indicators (even those relying only upon single phase properties) exhibit a significant lack of robustness, with their efficacy often being highly dependent upon the alloy class in question, or being limited to specific compositional domains. These issues can largely be tied to a general neglect of said indicators to consider underlying bonding differences.

In this work, a comprehensive comparative analysis of kinetic, thermodynamic, and structural properties in the Cu_{50}Zr_{50} and Ni_{50}Al_{50} alloy systems is conducted using molecular dynamics simulation methods. A key focus of this study is the investigation of underlying connections between the nature of atomic level bonding, short and medium range ordering, and the evolution of structure and transport properties as the two model systems are quenched from the high temperature molten liquid state. While the two alloys under investigation possess similar atomic size ratios and have previously been shown to possess comparable diffusive transport rates in the
liquid and supercooled domains, they nonetheless belong to two separate classes of alloys; the transition metal - transition metal (TM-TM) and transition metal - metalloid (TM-M) classes respectively. As such, the combined analysis of Cu$_{50}$Zr$_{50}$ and Ni$_{50}$Al$_{50}$ alloys provides the ideal setting to explore fundamental limitations of the various existing GFA indicators and compositional tuning methods, and to potentially facilitate in the identification of new predictive parameters and influencing factors.

4.2 Computational Details

Molecular dynamics simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS [34]) software package, with atomic interactions described using many-body embedded atom method (EAM) interatomic potentials developed by Mendelev [47] and Mishin [35] for Cu-Zr and Ni-Al alloys respectively. Bulk liquid and glassy phases were generated by first heating randomly ordered systems of 8000 atoms from 300K to 2300K over a duration of 1000ps, followed by a 2000ps relaxation stage allowing for the proper equilibration of the high temperature liquid melt. Following equilibration, systems were subsequently cooled down to a temperature of 50K through a series of 25K quench(100ps) and hold(150ps) stages, corresponding to an average linear cooling rate of 0.1K/ps. Throughout the quenching process, zero pressure isobaric conditions were applied using NPT Nose-Hoover temperature and pressure controls under 1fs integration time-steps. Bulk crystalline phases for both systems were generated and relaxed (similarly under zero pressure barostatic conditions with a 1fs time-step) at relevant temperatures according to a B2 structured supercell containing 8470 atoms or 35x11x11 unit cells (following Tang and Harrowell [45]). For both phases in question, property extraction was conducted following further system relaxation at relevant temperatures of interest. Analysis of molecular dynamics simulations results were conducted externally in PYTHON, allowing for the calculation of transport, thermodynamic, and structural properties. More specifically, detailed thermodynamic modeling techniques were used to establish melt/liquidus temperatures and relative phase stabilities throughout the supercooled domain. Using this information, GFA indicators commonly used to quantify the relative phase stability of the amorphous phase such as the reduced glass transition temperature, $T_{rg}$, and the liquid-crystal free energy difference at glass transition, $(\Delta\mu)_{Tg}$, were extracted. Furthermore, volumetric data collected for the crystalline and disordered phases were used to investigate free
volume content through the calculation of fractional density differences between the respective phases, \((\rho_c - \rho_{liq})/\rho_c\). Viscous and diffusive transport properties were also sampled along the quenching process, allowing for the assessment of the kinetic fragility parameter, \(m\), and strength parameter, \(D^*\), both of which are common GFA indicators serving to differentiate between “strong” and “fragile” glasses based on how abrupt the viscous slowdown is on approach to \(T_g\). Each of these bulk system properties and parameters serve to quantify key influencing factors governing crystallization kinetics in general, the thermodynamic forces driving crystallization, and the kinetic factors controlling the rates of crystal nucleation and growth. On the atomic level, short and medium-range chemical and topological ordering was assessed over the quench domain through radical Voronoi tessellation and partial radial distribution function analysis. The evolutions of underlying bond anharmonicity and bulk stiffness properties were also investigated in order to assess underlying bonding differences that may elucidate underlying structure-property trends and GFA anomalies. In conjunction, vibrational density of states spectra were calculated in each system, allowing for a detailed analysis of underlying vibrational properties at the atomic level. Lastly, in an attempt to further connect local bonding differences with observed property trends, short-range cluster statistics were analyzed from a local energy perspective.

4.3 Results and Discussion

Molecular dynamics simulations of amorphous and B2 crystalline phases for both Ni-Al and Cu-Zr systems were conducted and sampled along the various temperatures of interest. Liquid and glassy phases were generated through rapid quenching of initial equilibrated melts at temperatures of 2100K and 2300K respectively for Cu-Zr and Ni-Al respectively (roughly encompassing a temperature domain up to \(3T_g\) for both systems). Thermodynamic, physical, transport, and structural properties were subsequently sampled (following 300ps relaxation runs) in 25K intervals as the system was quenched down to 50K, with results presented in the following sections.
4.3.1 Bulk Thermodynamic and Physical Properties

Figure 4.1: Gibbs Free Energy profiles for liquid/amorphous and B2 crystalline phase Cu-Zr (left) and Ni-Al (right) calculated from 2PT modeling. Vertical dashed lines correspond to respective $T_g$ values. Melting points ($T_m$) are identified by the intersection of liquid/amorphous and crystalline phases.

Gibbs free energy curves for the amorphous and crystalline phases are presented in Figure 4.1. Based on the point of intersection of liquid and crystal phase free energy curves, melting points are calculated to be 1557K and 1355K for the Ni-Al and Cu-Zr systems respectively. For quick validation of the 2PT modeling, these values seen to be in close agreement with Tang and Harrowell’s [45] estimates of 1535K and 1340K obtained through the condition of equilibrated coexistence for liquid and crystal phases in planar contact. Glass transition temperatures ($T_g$) of 740K and 676K for Ni-Al and Cu-Zr systems were extracted using enthalpy cooling curve data (see computational details). While experimental $T_g$ values for the Ni-Al system are unavailable due its rapid crystallization rate, Cu-Zr’s computed $T_g$ value is seen to be in direct agreement with Russeeu’s [30] experimentally determined $T_g$ value of 676K based on viscosity data.

Utilizing these results, reduced glass transition temperatures ($T_{rg}$) and liquid-crystal free energy differences at $T_g$, $\Delta \mu (T_g)$, were evaluated, yielding values of 0.48 and -0.116eV/atom for Cu-Zr, and 0.50 and -0.135eV/atom for Ni-Al. Comparison of these results (summarized in Table 4.1)
yields quantitative evidence for the lower thermodynamic phase stability of the Ni-Al amorphous phase.

**Table 4.1:** Summary of thermodynamic and bulk physical property results

<table>
<thead>
<tr>
<th></th>
<th>(T_g) [K]</th>
<th>(T_m) [K]</th>
<th>(T_{rg})</th>
<th>(\Delta h_m) [eV/atom]</th>
<th>(\Delta s_m) [eV/K·atom]</th>
<th>(\Delta \mu(T_g)) [eV/atom]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Al</td>
<td>744</td>
<td>1557</td>
<td>0.48</td>
<td>0.233</td>
<td>0.000150</td>
<td>-0.135</td>
</tr>
<tr>
<td>Cu-Zr</td>
<td>676</td>
<td>1355</td>
<td>0.50</td>
<td>0.200</td>
<td>0.000148</td>
<td>-0.116</td>
</tr>
</tbody>
</table>

Constant pressure heat capacities, \(C_p\), for Ni-Al and Cu-Zr amorphous phases are presented in Figure 4.2. The Ni-Al system undergoes a more dramatic \(C_p\) drop compared to Cu-Zr on approach to \(T_g\), indicating the freezing out of a higher density of states in the deeply supercooled domain [48]. Based on the energy landscape considerations of Angell, Ito, and Moynihan [49][50], the Ni-Al system would therefore be associated with a higher thermodynamic fragility than Cu-Zr, results consistent with existing correlations between thermodynamic/kinetic fragility and GFA.

![Heat Capacity of Amorphous Phase](image)

**Figure 4.2:** Constant pressure heat capacity, \(C_p\), of Ni-Al and Cu-Zr amorphous phases.

Harmonic approximations are used to partially account for low temperature \(C_p\) quantum contributions through the subtraction of \(3k_B\).
4.3.2 Transport and Kinetic Properties

![Amorphous Phase Viscosities](image)

**Figure 4.3:** Viscosity and atomic self-diffusivities for $\text{Ni}_{50}\text{Al}_{50}$ and $\text{Cu}_{50}\text{Zr}_{50}$ alloys over the quench regime

Results of calculated atomic diffusivities and shear viscosities are presented in Figure 4.3. In order to quantitatively assess kinetic fragilities, viscosity data were fit to the Vogel-Fulcher-Tammann (VFT) form:

$$\eta(T) = \eta_0 \exp\left(\frac{D^* T_0}{T - T_0}\right)$$ \hspace{1cm} (3.16)

Where $\eta_0$ is the high temperature viscosity limit, $T_0$ is the divergence temperature (often close in value to the Kauzmann temperature $T_K$), and $D^*$ is the strength parameter. Kinetic fragility parameters ((3.17)) were further estimated by interpolating viscosities down to a rheological glass transition temperature $T_g^{\eta=10^3\text{Pa}\cdot\text{s}}$ identified by the rheological condition that $\eta(T_g) = 10^3\text{Pa} \cdot \text{s}$ (see Methodology and Computational Details Section 3.4 for a detailed discussion of the physical basis for using this alternative viscosity condition instead of the standard rheological condition of $\eta(T_g) = 10^{12}\text{Pa} \cdot \text{s}$ which applies under experimental conditions). These results, in conjunction with estimated rheological glass transition temperatures ($T_g^{\eta=10^3\text{Pa}\cdot\text{s}}$), are summarized in Table 4.2 below.
### Table 4.2: Viscosity VFT Fit and Fragility Results

<table>
<thead>
<tr>
<th></th>
<th>(\eta_0) (10^{-4}\text{Pa} \cdot \text{s})</th>
<th>(T_0) [K]</th>
<th>(T_g^{\eta=10^3\text{Pa} \cdot \text{s}}) [K]</th>
<th>(D^*)</th>
<th>(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Al</td>
<td>9.77</td>
<td>650</td>
<td>748</td>
<td>2.07</td>
<td>61.4</td>
</tr>
<tr>
<td>Cu-Zr</td>
<td>15.22</td>
<td>617</td>
<td>690</td>
<td>1.58</td>
<td>75.5</td>
</tr>
</tbody>
</table>

Comparing strength and kinetic fragility parameters (\(D^*=2.07\) and 1.58, \(m=61.4\) and 75.5 respectively for Ni-Al and Cu-Zr), both values indicate the Ni-Al system to be the kinetically stronger system, an unexpected result considering Ni-Al’s lower GFA and thermodynamic fragility. Interestingly, as is illustrated by Cu-Zr’s significantly higher \(\eta_0\) value of \(15.2\times10^{-4}\text{Pa} \cdot \text{s}\) in comparison to Ni-Al’s \(9.8\times10^{-4}\text{Pa} \cdot \text{s}\), Ni-Al’s lower fragility is largely non-reflective of traditional correlations to high temperature melt atomic mobilities. Investigation into high temperature property variations revealed that near their respective melting points, Ni-Al diffusivities are about 1.6-1.7 times that of Cu-Zr, and Cu-Zr viscosities are approximately 1.2-1.3 times higher than Ni-Al. Quite surprisingly however, while Cu-Zr appears to possess lower atomic mobilities in the high temperature melt, a dramatic drop in Ni-Al transport rates is observed upon entering the supercooled domain, resulting in lower atomic mobilities for Ni-Al throughout much of the supercooled temperature region, and subsequently, a lower kinetic fragility. Further compounding these discrepancies, accounting for the approximately 10 percent shorter (average) atomic jump distances expected in the Ni-Al system (due to the smaller atomic radii of Ni and Al in comparison to Cu and Zr), transport rates for the Ni-Al system are effectively underrepresented. This can more clearly be seen by scaling atomic diffusivities by associated squared atomic radial distances, with the results of such scaling illustrated in Figure 4.4 (with temperatures also scaled by respective \(T_g\) values). While also apparent in the unscaled diffusivity plots, scaled Zr atomic diffusivities are seen to be significantly lower than Cu atoms, indicative of enhanced decoupling between diffusive and viscous transport in the Cu-Zr amorphous phase (Stoke-Einstein breakdown) and likely reflective of more collective flow behavior.
Investigating thermal stabilities through a kinetic perspective, fractional density differences \( \left( \frac{\rho_{c} - \rho_{liq}}{\rho_{c}} \right) \) between respective amorphous and crystalline phases are calculated over relevant temperatures of interest and plotted in Figure 4.5. Based on free volume theory, one would expect the higher atomic mobilities observed for Ni-Al in the high temperature melt regime to correspond with poorer atomic packing efficiencies and higher free volume content. These notions are consistent with the fractional density differences calculated, with results revealing the presence of anomalously large volume differences between the Ni-Al amorphous and crystalline phase. Summarized in Table 4.3, fractional liquid-crystal density differences observed for the Ni-Al system range from 7 – 11% along the quench, corresponding to values 2-3 times that of the Cu-Zr system. The 10% volume change observed at \( T_{m} \) in the Ni-Al system marks a significant departure from the 0 – 3% volume change characteristic of good glass forming systems [33][51]. With that said, these results are suggestive of primarily kinetic origins to Ni-Al’s poor GFA, likely associated with underlying bond frustration and packing inefficiencies in the amorphous phase.
Table 4.3: Fractional liquid-crystal density difference at $T_g$ and $T_m$

<table>
<thead>
<tr>
<th></th>
<th>$\frac{\Delta \rho_{le}}{\rho_c} (T_g)$</th>
<th>$\frac{\Delta \rho_{le}}{\rho_c} (T_m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Al</td>
<td>7.60 %</td>
<td>10.04 %</td>
</tr>
<tr>
<td>Cu-Zr</td>
<td>2.75 %</td>
<td>4.08 %</td>
</tr>
</tbody>
</table>

The lower kinetic fragility of the Ni-Al system is a significant result considering the previous thermodynamic fragility analysis as well as existing fragility-GFA correlations. Considering the remarkably large fractional volume differences observed between Ni-Al amorphous and crystal phases, along with the significant volume contraction experienced over the quench domain, the observed transport property trends in the Ni-Al system may be explained by consideration of the inter-atomic interaction changes and associated bond-strain effects. In order to explore test this concept, bulk moduli ($B$), constant volume heat capacities ($C_v$), and thermal expansion coefficients ($\alpha_T$) were independently calculated, allowing for the calculation of amorphous phase Gruneisen parameters ($\gamma$) through the following thermodynamic relation:

$$\gamma = \frac{\alpha_T B}{C_v \rho}$$

(3.7)

The Gruneisen parameter quantifies underlying bonding stiffness (or vibrational frequency) dependencies on volume/strain and is defined as:

$$\gamma = -\frac{V}{\omega} \frac{d\omega}{dV} = -\frac{r}{6k} \frac{dk}{dr}$$

(4.1)

where $\omega$ is the phonon frequency, $k$ is the interatomic force constant (bond stiffness), $V$ is the volume, and $r$ is the inter-atomic separation. As noted by Fultz [52], assuming a Gruneisen parameter $\gamma \approx 2$, the above relations would subsequently predict an inter-atomic force change of -12% given an inter-atomic distance change of only 1%. As such, the Gruneisen parameter is highly relevant to the analysis of bonding in the amorphous phase where inter-atomic separation distances are variable from atom to atom.
First focusing on resultant property variations in the liquid and supercooled domains (see Figure 4.6), Cu-Zr Gruneisen parameters are found to undergo a near monotonic decay from the high temperature value of $\gamma \approx 1.65$, down to a value of $\gamma \approx 1.35$ at the glass transition temperature. Such a monotonically decreasing profile would be expected should the underlying structural and chemical reordering taking place over the quench be conducive to the improvement of atomic level bonding and packing configurations (thereby leading to reduced bond strain and anharmonicity). In contrast, the Ni-Al system experiences the opposite Gruneisen parameter trends. Ni-Al Gruneisen parameters are seen to increase from $\gamma \approx 2.0$ up to a maximum of approximately 2.5-3.0 just above $T_g$, followed by a sudden drop to a value of $\approx 2.05$ at $T_g$. These differences continue down into the low temperature glassy domains where the monotonically decreasing Gruneisen profile observed in the Cu-Zr melt domain is observed to continue down to minimum of $\gamma \approx 0.9$, while Ni-Al Gruneisen parameters more or less persist at a constant value of $\gamma \approx 2.0$. Interestingly, clear differences are also observed upon comparison of respective bulk moduli profiles. Nearly identical Ni-Al and Cu-Zr bulk moduli are observed down to temperatures of about $1.3T_g$, upon which a sudden departure is observed among the two systems. Near $T \approx 1.3T_g$, a sudden bulk moduli increase persisting down to $T_g$ is observed in the Ni-Al system, indicative of substantial changes in underlying stiffness and bonding properties. It is apparent that $1.3T_g$ also corresponds to peak thermal expansion coefficients, and thus to the region of greatest volumetric temperature sensitivity and contraction. Combined, these results
suggest a strong connection between relaxation properties and underlying mechanical ordering associated with bond anharmonicity and strain-volume dependencies in the Ni-Al system. In accordance with the large Gruneisen parameters observed in the Ni-Al system, the large volume contraction observed over the supercooled domain would have the side effect of substantial bond stiffness increases, ultimately reflected through higher structural relaxation times near $T_g$ and a correspondingly lower fragility. In the high temperature melt, the Ni-Al system likely experiences significant local bond strain and mismatch as evidenced by fractional liquid-crystal volume differences in excess of 10%, in contrast to volume differences 2-3 times lower in the Cu-Zr system.

![Graphs](image)

**Figure 4.6:** Second order thermodynamic properties and resultant Gruneisen Parameters for Ni$_{50}$Al$_{50}$ and Cu$_{50}$Zr$_{50}$ amorphous phases over the quench regime

Cu-Zr and Ni-Al systems belong to two separate classes of alloys, so the question arises as to whether the observed anharmonicity and bonding differences can be generalized to be attributes of TM-TM and TM-M bonding as a whole, or whether they are specific to the given alloys in question. A reasonable expectation would be for the observed differences in bonding, transport, and kinetic properties to be reflected in the nature and evolution of short and medium range
structure over the quench. To test this hypothesis, an in-depth investigation of short/medium-range chemical and topological ordering is conducted in the following section, largely aimed at the search for key structural signatures of underlying bonding differences.

4.3.3 Structural Analysis

![Figure 4.7: Pair Correlation Functions evaluated for $\text{Ni}_{50}\text{Al}_{50}$ and $\text{Cu}_{50}\text{Zr}_{50}$ melts at temperature $T \approx 2 \times T_g \approx T_m$](image)

In order to assess medium-range ordering differences, pair correlation functions were computed for both systems, with results evaluated near respective melt temperatures (1400K and 1600K for Cu-Zr and Ni-Al respectively) presented in Figure 4.7. Analyzing the figures, density correlations extending from the nearest-neighbour to next-nearest-neighbour coordination shells are seen to much more rapidly decay in the Ni-Al system, most notably apparent upon comparison of the ratio of first and second peak heights (summarized in Table 4.4) for Ni-Al and Cu-Zr pair-correlation functions (3.05 and 2.50 respectively). In conjunction with these observations, the high first peak intensities and large extent of bond-length shortening observed suggest significantly more pronounced Ni-Al nearest-neighbour level interactions. Looking beyond the first peak, relatively weak Ni-Ni, Ni-Al, and Al-Al density correlations with nearly identical profiles are observed, indicating a low degree of medium-range compositional ordering. In contrast, longer-ranged next-nearest-neighbour interactions appear much more pronounced in the Cu-Zr system, with strong and largely non-overlapping density correlations extending well into the 2nd, 3rd, and even 4th coordination shells.
Table 4.4: Ratio of first and second partial radial distribution peak intensities

<table>
<thead>
<tr>
<th></th>
<th>$g_{AA}(r_1)/g_{AA}(r_2)$</th>
<th>$g_{AB}(r_1)/g_{AB}(r_2)$</th>
<th>$g_{BB}(r_1)/g_{BB}(r_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Al</td>
<td>1.78</td>
<td>3.05</td>
<td>1.92</td>
</tr>
<tr>
<td>Cu-Zr</td>
<td>1.70</td>
<td>2.50</td>
<td>1.92</td>
</tr>
</tbody>
</table>

These observations are consistent with metal-metal (TM-TM) and metal-metalloid (TM-M) bonding in general. Belonging to the TM-TM alloy class (and associated with copper’s noble metal electronic state), Cu-Zr bonding would be expected to be longer-ranged and less directional. In contrast, TM-M bonding is characteristically more covalent/short-ranged and directional, consistent with the observed Ni-Al bond-length shortening, pronounced nearest-neighbour level interactions, and weak next-nearest-neighbour interactions. Thus, a simple phenomenological explanation for the observed Gruneisen and bulk moduli anomalies in the Ni-Al system can be formulated based on these expected bonding differences. Mismatch between underlying strain-stiffness dependencies of Ni-Al, Ni-Ni, and Al-Al partial bonds inhibits bulk structural relaxation to globally efficient packing structures in the high temperature Ni-Al melt. Subsequently, the high temperature Ni-Al melt exhibits high free volume content and high diffusive and viscous transport rates. As the system is cooled, associated volume contraction results in significantly increased interactions among previously “non-bonded” or poorly bonded Ni-Al atoms, translating to a sudden spike in bulk stiffness properties (bulk moduli), viscosities, and ultimately to a lower kinetic fragility. Bonding in the Cu-Zr system is longer-ranged, less directional, and highly metallic in character, translating to minimal short-range bonding constraints, and promoting global structural relaxation (through more cooperative flow rearrangements) to lower free volume packing configurations. While the Ni-Al system exhibits a lower kinetic fragility than Cu-Zr, it is largely an artifact of the underlying volume-strain and bond-stiffness dependencies. As previously noted by Suranarayana and Inoue [53], the efficacy of the fragility parameter as a direct measure of GFA is highly dependent upon the respective alloy class in question. While the fragility (strength) parameter $D^*$ has been identified to act as a direct measure of GFA in BMGs with purely metallic components [54][55], it largely breaks down as a reliable GFA indicator in systems containing metalloid species.
Figure 4.8: Top 25 most frequent Voronoi polyhedra types in Ni-Al and Cu-Zr Glasses at 300K

Figure 4.9: Partial and Total Coordination Number Distribution for atoms in Ni-Al and Cu-Zr Glasses at 300K
Results of radical Voronoi tessellation analysis of short-range topological and compositional ordering in the two systems were similarly found to be reflective of such underlying bonding differences. Starting with nearest-neighbour cluster/polyhedra and coordination number distributions in respective Ni-Al and Cu-Zr glasses at 300K, results are presented in Figure 4.8 and Figure 4.9. At first glance, cluster and coordination distributions in respective glassy phases appear strikingly similar. However, further inspection reveals a number of differences reflective of the short-range versus long-range bonding properties of Ni-Al and Cu-Zr systems. Higher icosahedral ordering is observed in the Cu-Zr system (a signature of longer-ranged interactions and enhanced thermal stability of the amorphous phase), with higher fractions of $<0,0,12,0>$, $<0,2,8,2>$, and $<0,2,8,1>$ clusters. The coordination distributions in the Cu-Zr system are also seen to be more tightly distributed among CN=12 for Cu, and CN=16 for Zr atoms, with less respective coordination overlap and CN=14 clusters overall in comparison to the Ni-Al system. Considering the B2 crystal phase is entirely composed of CN=14 short-range clusters, these observations are suggestive of enhanced compositional ordering in the Cu-Zr system, with greater short-range structural overlap between the amorphous and crystal phases in the Ni-Al system.

Further inspection of resultant frequency distributions indicates that the top 7 most frequent polyhedra comprise a significant fraction of the total population (approximately 34% and 35% of the Al and Zr centered distributions, and about 45% and 55% of the Ni and Cu centered distributions respectively). Subsequently, short-range structural evolution over the transition from the high temperature melt down to the low temperature glassy phase was investigated by tracking the 7 most frequent polyhedra types found in the respective glassy phases. Viewing the results of this analysis (presented in Figure 4.10), an abrupt and dramatic increase in icosahedral-type clusters $<0,0,12,0>$, $<0,2,8,1>$, and $<0,2,8,2>$ is observed upon entering the supercooled domain for Cu-centred clusters. In both systems, the temperature onset for short-range structural reordering towards increased polytetrahedral cluster-types (i.e. polyhedra with high fractions of 5-edged faces) appears to strongly correlate with respective melting temperatures $T_m$. These observations are consistent with the similarly dramatic increase in the fraction of $<0,0,12,0>$ polyhedral observed between liquidus and glass transition temperatures in Cu$_{45}$Zr$_{47}$Al$_7$, Cu$_{46}$Zr$_{54}$, and Cu$_{45}$Zr$_{47}$Al$_7$ liquid alloys [31]. The nature of this correlation is likely tied to universal changes in the energy landscape topology occurring near the mode-coupling temperature of
liquid alloys. Combined, these considerations raise the possibility of rapidly estimating liquidus/melting temperatures of arbitrary multicomponent alloys based on short-range structural considerations alone, which if deemed to be viable, could yield immense value to GFA compositional tuning through the rapid estimation of predictive indicators such as the reduced glass transition temperature.

**Figure 4.10:** Frequency evolution of the 7 most frequent Voronoi Polyhedra types found in Ni-Al and Cu-Zr Glasses. Purple and blue dashed lines are presented to indicate glass transition and melt temperatures respectively (Note: legend indexed in decreasing order from top to bottom with respect to polyhedral fractions in low temperature glass).
**Figure 4.11:** Temperature evolution of mean partial coordination numbers for species in Ni-Al and Cu-Zr alloys over the quench.

**Figure 4.12:** Evolution of local compositional ordering over the quench for Cu-Zr and Ni-Al alloys. The Warren-Cowley parameter is a simple metric quantifying the deviation of the local composition (first coordination shell) from the bulk stoichiometric concentration.
Moving onto the analysis of the evolutions of mean local compositional environments of Ni, Al, Cu, and Zr centered atoms over the quench domain, results are presented in Figure 4.11. In contrast to the Ni-Al system, an apparent tendency towards enhanced Cu-Zr and Zr-Cu coordination in the Cu-Zr liquid melt is observed upon quenching down towards T_g. Further investigating compositional short-range ordering (CSRO), the evolution of the Warren-Cowley parameter [42] has been evaluated in both systems over the quench domain, with results presented in Figure 4.12. The Warren-Cowley parameter serves as a common metric for CSRO, with large (negative) values being indicative of significant deviations of local compositions from bulk stoichiometry (see section Methodology and Computational details: Structural Property Calculations as well as reference [42] for further details on the Warren-Cowley parameter). Significantly enhanced CSRO is apparent in the Cu-Zr system. While associated chemical reordering taking place in the Cu-Zr system is seen to freeze out at T_g as expected, the corresponding freeze-out temperature in the Ni-Al system is seen to occur near 950-1000K or \( \approx 1.3T_g \). Referring to Figure 4.6, it is apparent that the observed Ni-Al CSRO freeze-out temperature coincides instead with the bulk moduli departure temperature (as well as the temperature domain associated with peak expansivity). Subsequently, the strong bond strain-stiffness dependencies previously identified in the Ni-Al system are seen to have the negative side-effect of inhibiting compositional short-range ordering in the amorphous phase, a likely contributing factor to Ni-Al’s lower GFA.

4.3.4 Inspection of Nearest-Neighbour Structural Relaxation Properties

In order to further inspect relative interaction strengths between A-A, A-B, and B-B nearest-neighbour bonds in the two systems (A = Cu, Ni; B = Zr, Al), a bond correlation function \( C_{\alpha\beta}(t) \) is introduced which tracks the probability that a nearest-neighbour bond between atoms of type \( \alpha \) and type \( \beta \) will maintain after a duration of time \( t \). In order to calculate \( C_{\alpha\beta}(t) \), positions were sampled periodically over a duration of 130ps, and at each time-step \( t \), Voronoi tessellation was used to obtain the adjacency matrix \( A(t) \) which contains connectivity information between all \( N \) atoms in the system:

\[
A(t) = \begin{pmatrix}
a_{1,1}(t) & a_{1,2}(t) & \cdots & a_{1,N}(t) \\
a_{2,1}(t) & a_{2,2}(t) & \cdots & a_{2,N}(t) \\
\vdots & \vdots & \ddots & \vdots \\
a_{N,1}(t) & a_{N,2}(t) & \cdots & a_{N,N}(t)
\end{pmatrix}
\]

where \( a_{i,j}(t) = \begin{cases} 1 & \text{if atoms } i, j \text{ are neighbours} \\ 0 & \text{if } i, j \text{ are not neighbours} \end{cases} \)
\( C_{\alpha\beta}(t) \) is then calculated by summing \( a_{ij}(t) \cdot a_{ij}(0) \) over all \( i,j \) elements with atoms \( i \) belonging to type \( \alpha \) and atoms \( j \) to type \( \beta \):

\[
C_{\alpha\beta}(t) = \frac{\sum_{i \in \alpha} \sum_{j \in \beta} a_{ij}(t) \cdot a_{ij}(0)}{\sum_{i \in \alpha} \sum_{j \in \beta} a_{ij}(0) \cdot a_{ij}(0)}
\] (4.2)

Results for total and partial bond correlation functions for Ni-Al and Cu-Zr alloys in the liquid and supercooled domain are presented in Figure 4.13. Visually inspecting the results, standard stretched exponential relaxation profiles are evident for both systems, with a general divergence of mean relaxation times upon cooling into the heavily undercooled domain. In both systems, bond correlations for the smallest species elements (Cu-Cu and Ni-Ni) show the most rapid decay, suggesting weaker interactions between the smaller species. In the Ni-Al system, Ni-Al partial bond correlations appear to show the slowest decay rates, signifying stronger nearest-neighbour level interactions relative to Ni-Ni and Al-Al bonds. In the Cu-Zr system, one can see nearly identical partial bond correlations for Zr-Zr and Cu-Zr bonds, with Zr-Zr partial correlations displaying a marginally slower decay rate. As can be seen through the evolution of mean coordination environments plotted in Figure 4.11, the Cu-Zr system exhibits less Cu-Cu and more Cu-Zr nearest-neighbours as compared to Ni-Ni and Ni-Al coordination in the Ni-Al system. Interestingly, as the Cu-Zr system is cooled, significant chemical reordering is evident towards increased fractions of the “stronger” (longer relaxation time for bond-breaking) bonding species, which can be seen through reordering towards lesser Cu-Cu and higher Cu-Zr/Zr-Cu nearest neighbour bonding. The relative ratios of Ni-Ni, Ni-Al/Al-Ni, and Al-Al nearest neighbour bonds is much more constant during temperature evolution of the Ni-Al system, with a more controlling trend towards reduced total coordination being evident (likely in connection to the significant degree of volume contraction experienced in the Ni-Al system).
Figure 4.13: Total and partial bond correlation functions for Ni-Al and Cu-Zr alloys in the liquid and supercooled domain. Dashed lines in the partial bond correlation function plots correspond to 900K, with solid lines corresponding to 1200K.

4.3.5 Local Structure-Energy and Coordination-Energy Correlations

Interestingly, viewing Mishin’s [35] EAM embedding functions (reproduced below in Figure 4.14) for Ni and Al atoms, the Ni embedding function is seen to exhibit a minima near mean electron densities (as defined in (3.4)) in accordance with the traditional convex parabolic shaped profile characteristic of metallic elements. In contrast, at mean electron densities, the Al embedding energy function is seen to exhibit a maximum, with an apparent minima present in the low density regime, and a sharp decreasing profile observed in the higher density regime. These observations further elucidate underlying bonding differences, and are suggestive of highly variable bonding/stiffness properties of Al depending on bond strain and local coordination/compositions. The Al embedding function minima present in the lower density regime is likely to be the source of the poor amorphous phase packing efficiencies observed in the Ni-Al system, with the bulk moduli spike observed being associated with volume/strain...
contraction linked to the sharp decreasing energy profile in the higher local electron density domain. Considering the previous analysis of structural, kinetic, and bonding property differences in the two systems, Ni-Al bond-length shortening and mismatch between underlying strain-stiffness dependencies of Ni-Al, Ni-Ni, and Al-Al partial bonds introduce significant local bonding constraints which act to inhibit bulk structural relaxation and the attainment of globally efficient packing structures in the amorphous phase. The more metallic (non-directional, longer-ranged) bonding properties of the Cu-Zr system promote more collective relaxation behavior and drive topological and chemical reordering towards locally and globally efficient packing configurations. An interesting question is whether such bonding differences are discernible through the analysis of local, per-atom potential energies. Probing the degree at which local energetics influences short-range structural ordering in the two systems, statistics on the local atomic potential energies of atoms were collected and analyzed at various temperatures of interest along the quench. Subsequently, mean (local atomic) potential energies for central atoms belonging to the various Voronoi polyhedra types sampled were evaluated, and correlations with Voronoi polyhedra occupation probabilities (cluster distributions) were assessed.

**Figure 4.14:** Mishin’s EAM embedding energy functions for Ni and Al atoms in the equilibrium B2-Ni-Al phase [35]
Viewing the results of this analysis for Ni, Al, Cu, and Zr centered clusters at 1200K presented in Figure 4.15 above (other temperatures displayed similar results), a number of notable differences/features are apparent. Firstly, overall short-range cluster distributions appear to follow a Boltzmann distribution, with the probability of an atom being attributed to a cluster of Voronoi type \(<n_3,n_4,n_5,\ldots>\), \(P_{<n_3,n_4,n_5,\ldots>}\), being exponentially dependent upon the mean potential energy, \(\overline{PE}_{<n_3,n_4,n_5,\ldots>}\), of central atoms in respective clusters:

\[
P_{<n_3,n_4,n_5,\ldots>} \propto \exp\left(\frac{-\overline{PE}_{<n_3,n_4,n_5,\ldots>}}{k_B T}\right) \tag{4.3}
\]

Significantly greater scatter is evident for the Cu-Zr system in comparison to the Ni-Al system. Ni short-range cluster probabilities also appear heavily influenced by local energies, with significant energetic differences observed between the highest and lowest probability cluster types. While not conclusive, these differences support previous bonding considerations. The more short-range/covalent character of Ni-Al partial bonds and underlying mismatch between strain-stiffness dependencies of Ni-Al, Ni-Ni, and Al-Al partial bonds are expected to largely constrain local bonding configurations, with certain local geometric configurations being highly favorable (low-energy) and others unfavorable (high-energy). In contrast, longer-ranged interactions in the Cu-Zr system would be expected to result in a higher relative influence of next-nearest-neighbour atomic configurations on local atomic potential energies. The more metallic, non-directional bonding properties of the Cu-Zr system would likely promote more collective rearrangement and relaxation behavior, further weakening the correlations between local cluster energies and probabilities.
Relative sampling frequencies for different local coordination sets [CN_A, CN_B] about central atoms of type A and B were also collected for both Ni-Al and Cu-Zr systems at 300K in the glassy phase. In addition, mean potential energies for central atoms in clusters of various coordination environments were calculated, allowing for further analysis of local energy correlations (with results presented in Figure 4.16 and Figure 4.17). A number of interesting observations can be made which further elucidate underlying bonding differences in the two systems. Firstly, significantly less overlap is observed between coordination-set domains of high frequency and those of low mean potential energy for Cu and Zr species in the Cu-Zr system relative to Ni and Al atoms in Ni-Al. This is particularly apparent upon comparison of Cu’s frequency distribution and coordination-energy plots for which the minimal energy coordination region is located about [CN_Cu = 12, CN_Zr = 0], while the associated Cu coordination-energy plot is centred far away, broadly about [CN_Cu = 8, CN_Zr = 5]. Examination of the Zr coordination-
energy plot revealed linear energy contour lines along coordinations of equivalent total coordination number, \(CN_{\text{tot}}\), up to a total coordination numbers of \(CN_{\text{tot}} = 18\), with higher total coordinations being associated with lower local Zr potential energies. In contrast, such tendencies are largely absent in the Al energy plots.

**Figure 4.16:** Local coordination-frequency and local coordination-energy correlations for Cu and Zr centered atoms.
While the previous Voronoi analysis of short-range structure and compositional ordering in the two systems indicates relatively similar short-range cluster and coordination distributions, one see that the two systems exhibit strikingly different local energetics. Overall, it is apparent that ordering in the Cu-Zr system is much less constrained by local bonding configurations, geometry, or coordination. Under the presence of significantly less nearest-neighbour bonding constraints, and the strong favorability of Zr towards higher total coordinations, ordering in the Cu-Zr system is seen to be much more controlled by larger scale energetics, likely driving the system toward lower free-volume amorphous packing configurations. Within this context, entropic factors (such as mixing disorder) and atomic size mismatch are likely to play a much more significant role in dictating crystal nucleation and growth kinetics in the Cu-Zr system,
potentially explaining the huge disparity in glass forming ability observed with respect to the Ni-Al system.

4.3.6 Investigating the Connections between the Vibrational Properties, Fragility, and Glass Forming Ability of Alloys

Reflecting upon the significant overlap in Voronoi short-range cluster distributions observed in the Cu-Zr and Ni-Al amorphous systems, it is clear that the stability of the amorphous phase is to a large degree dependent upon the nature of larger scale ordering/packing, and more importantly, atomic level bonding properties including next-nearest-neighbour and other longer-ranged bonding/ordering interactions. The inability of nearest neighbour structural analysis methods (such as Voronoi tessellation) from inferring the strength or degree at which nearest-neighbour atoms are bonded can therefore be seen to be a serious deficiency limiting the ability to infer global amorphous phase stability, particularly in cases where local bonding properties are heavily compositionally or geometrically dependent (as is the case for Ni-Al or other systems with similar covalent bonding character). While the previously discussed Gruneisen parameter temperature variation trends, RDF analysis, and local cluster-energy correlations provided significant evidence for this, further insight into the nature of these underlying bonding differences can be gained through the analysis of vibrational properties in the two systems. Calculated vibrational density of states (VDOS) spectra are presented below (see Figure 4.18) for further analysis of bonding and stiffness properties in the amorphous and B2 crystalline phases.

![Figure 4.18: Vibrational DOS Spectra for elemental components in Cu-Zr and Ni-Al B2-crystalline and Glassy phases](image)
Firstly, a clear band-gap is observed in the Ni-Al B2-crystal phase VDOS, with Al atoms primarily occupying the higher frequency (optical) bands, and Ni atoms primarily occupying the lower frequency (acoustic) bands. In contrast, the band gap is largely absent in the Cu-Zr VDOS, and significantly more pronounced Cu and Zr vibrational spectra overlap is displayed. Similar segregation of Al to higher frequency vibrational modes and Ni to lower frequency vibrational modes is evident in the Ni-Al amorphous phase, with even more pronounced overlap being observed between Cu and Zr vibrational spectra in the Cu-Zr amorphous phase. At least in the case of the Ni-Al system, the observed segregation of Ni and Al atoms into well separated acoustic and optical bands can largely be understood by considering the simple analogy to the linear diatomic chain model. Denoting the A-B bond stiffness (or spring constant), k, the atomic lattice spacing, a, the mass of type A and B atoms, \( M_A \) and \( M_B \), and the reduced mass, \( \mu \):

\[
\mu = \frac{1}{\frac{1}{M_A} + \frac{1}{M_B}}
\]  

(4.4)

Resultant phonon dispersion curves \( \omega(q) \) (where \( q = 2\pi/\lambda \) is the wavevector) for the 1-d diatomic chain are plotted below in Figure 4.19 for the case of \( M_A = M_{Ni} = 58.68u \), and \( M_B = M_{Al} = 26.98u \). For the simplistic case of a 1d Ni-Al diatomic chain with only nearest-neighbour interactions, the large mass difference between Ni and Al can be seen to result in two well separated branches: the acoustic branch which goes to zero at small wave-vectors (\( \omega(q) \to 0 \) as \( q \to 0 \)), and the higher frequency optical branch for which \( \omega(0) \neq 0 \). Modes at the brillouin zone (\( q = \pi/a \)) can simply be interpreted to involve the movement of only one out of two atoms in the sublattice, thereby resulting in a vibrational frequency of either \( \sqrt{(2k/M_A)} \) or \( \sqrt{(2k/M_B)} \). Similarly, the motion of atoms for vibrational modes at small q (\( q \to 0 \)) are nearly identical (exactly identical for \( q=0 \)) from unit cell to unit cell, and can be interpreted to describe the dispersion-free propagation of sound waves for the acoustic branch, or the vibration of heavy (A) and light (B) atoms in an identical fashion for each unit cell in the optical branch (which can be further reduced to a vibrating atom of reduced mass, \( \mu \), with force-constant, 2k). Considering the cubic B2 crystal unit cell with atoms of type B at the corner edges and A in the center, it can be seen that such an analogy is exact for wave-vectors pointed in the (111) directions where nearest neighbour atoms alternate in an ABAB fashion. In this sense, the segregation of Al atoms to high frequency optical bands, and Ni to lower frequency acoustic bands is further suggestive of strong/stiff short-ranged nearest-neighbour Ni-Al interactions. Interestingly, while one would
expect lower frequency bands for the Cu-Zr system based on the fact that Zr is significantly heavier than Al (91.22u vs. 26.98u), as well as a smaller band gap due to the smaller relative mass difference between Cu and Zr (63.55u vs. 91.22u). Cu and Zr vibrational spectra in the B2 phase appear strikingly similar with significantly overlapping profiles, further suggestive of next-nearest-neighbour interactions playing a more dominating role in the Cu-Zr system.

![1-d Diatomic Chain](image)

**Figure 4.19:** Phonon dispersion curve for a model 1-dimensional diatomic chain with bond-stiffness, k, between components A and B of mass, M_A and M_B, and reduced mass \( \mu \).

Comparing VDOS spectra for amorphous and B2-crystalline phases, both Ni-Al and Cu-Zr amorphous phase VDOS are seen to display excess spectral density beyond that of the standard \( g(\omega) \propto \omega^2 \) Debye-like scaling relationship expected (of crystalline materials) in the low frequency domain. This can more easily be seen by plotting the reduced VDOS spectrum \( g(\omega)/\omega^2 \) (see Figure 4.20), where this excess spectral density in the amorphous phase is clearly identified as a peak in the low frequency domain, called the “boson peak”. The boson peak is characteristic of the glassy phase, and recently [17][18] has been tied to an underlying topological phase transition in the in the potential energy landscape, from a region dominated primarily by saddle points above mode coupling temperature, \( T_{MC} \), to one dominated by minima at lower temperatures. These findings have indicated that above \( T_{MC} \), the nearest stationary points or generalized inherent structures (GIS) visited through means of steepest descent energy minimization are saddle points (potential energy Hessian at the critical point possesses at least one negative eigenvalue), subsequently, diffusion and atomic transport in this region.
predominately occurs along unstable directions of saddles. Below $T_{MC}$, a topological phase transition occurs to a phase space domain whose nearest stationary points correspond to local potential energy minima (all positive energy Hessian eigenvalues), with phonons predominating in this low temperature phase while being absent in the high temperature phase above $T_{MC}$.

Within this context, the boson peak appears in the VDOS spectrum as a signature of a transition from the low temperature phonon phase exhibiting a Debye $g(\omega) \propto \omega^2$ scaling, to a $g(\omega) \propto \omega^\gamma$ ($\gamma < 2$) phase associated with the softening of acoustic modes on approach to the phonon-saddle transition at $T_{MC}$ [17][18]. Boson peak positions, $\omega_{BP}$, are predicted to shift to lower frequencies as the critical point is approached according to a simple, $\omega_{BP} \propto \Delta^{-\rho}$, scaling relationship, where $\Delta = T_{MC} - T$ (or equivalently $\Delta = e_c - e_{IS}$ where $e_c$ represents the mean equilibrium inherent structure energy $e_{IS}$ sampled at mode coupling temperature $T_{MC}$). Boson peak heights, $g(\omega_{BP})$, are similarly predicted to follow a simple scaling law as a function of the distance away from the critical point, $g(\omega_{BP})/\omega^2 \propto \Delta^{-\beta}$. Amazingly, the phonon-to-saddle transition in metallic glasses belong to a greater universality class of critical phenomena, and as such, are predicted to share a common set of critical exponents, with $\rho \approx 1$, $\gamma \approx 3/2$, and $\beta \approx 1/2$. Interestingly, further investigations of the nature of the lowest 1% frequency vibrational modes in glasses have revealed strong connections with localized soft-spots, localized structural rearrangements, beta-relaxations, and shear transformation zones. Ding et. al.’s [56] investigation of the participation fraction of central atoms in various Voronoi cluster types in the Cu$_{64}$Zr$_{36}$ system revealed significant short-range structural variation between different polyhedra types, with certain geometrically unfavorable motifs (GUMs) highly contributing, while other cluster types such as the icosahedral $<0,0,12,0>$ and the Kasper polyhedra provided significant structural rigidity with minimal participation fractions. Considering the significant short-range cluster/coordination-energy correlation differences observed in the Ni-Al and Cu-Zr systems, it is likely that many of the geometrically favorable motifs contributing to structural rigidity in one system may in fact be unfavorable in the other, further outlining the importance of considering fundamental bonding properties at the atomic level.
Figure 4.20: reduced vibrational density of states spectra for the display of low frequency boson peaks

Comparing amorphous phase VDOS spectra, one can note significantly higher boson peak heights as well as as lower frequency peak positions, $\omega_{BP}$, in the Cu-Zr system. While not conclusive, it is possible that these results are reflective of the Cu-Zr glassy phase being frozen into a state in closer proximity to the critical point, or alternatively, a significantly smaller temperature difference, $\Delta T_g = T_{MC} - T_g$. Partial spectra for Cu and Zr species are also seen to display significantly greater similarity relative to Ni and Al in the Ni-Al system, likely due to the greater atomic mass mismatch in the Ni-Al system. These observations raise a number of interesting questions that may potentially have long reaching implications in the field of compositional tuning and glass forming ability. For one, the mode coupling temperature $T_{MC}$ of alloy melts is often correlated with melting temperature $T_m$ in many alloy systems. Considering the correlations observed between glass forming ability, reduced glass transition temperature $T_{rg} = T_g/T_m$, and fragility $m$, an interesting prospect is the use of energy landscape sampling for the direct estimation of $T_{MC}$ for use in an alternative correlator (which can be called the “reduced Mode Coupling temperature”) $T_{rmc} = T_g/T_{MC}$. Should such a parameter correlate with GFA
independently, it may serve as a valuable compositional tuning parameter, especially in multicomponent alloys for which little is known regarding the nucleating phases or melting points.

Furthermore, while considerable progress has been made in the compositional tuning front through the consideration of simple parameters such as the atomic size ratio, an interesting prospect is that associated failures of such methods in TM-M methods (i.e. Ni-Al) may be linked to underlying vibrational property differences. In specific, it may be worth investigating the associated contributions to GFA/atomic-size ratio correlations associated with differences in underlying atomic-mass ratios. While size and mass ratios are correlated in many systems, this correlation is likely to break down in cases where bonding is highly directional and covalent (such as the Ni-Al system were Ni possesses a much larger relative mass, while simultaneously possessing the smaller atomic radii), resulting in significant differences in underlying vibrational properties. The significantly higher vibrational frequencies observed in the Ni-Al system due the large atomic mass mismatch between Ni and Al atoms may potentially be a significant contributing factor to the anomalous low fragility relative to the Cu-Zr system. The observed spike in bulk stiffness properties observed near 1.3Tg in the Ni-Al amorphous melt are likely to correspond to a significant transition to higher vibrational frequencies. Considering recent findings connecting the vibrational properties of liquids and glasses with viscous transport and structural relaxation properties (under a universal scaling relationship) of the melt under ACS theory [57], this sudden spike in vibrational frequencies would be expected to result in a corresponding increase in structural relaxation kinetics (essentially due to an increased attempt frequency), which would subsequently result in a dampening of the viscosity slowdown process on approach to Tg, and a superficially low kinetic fragility. Clearly, the lower fragility in this situation is not going to have the same relative impact on GFA.

4.3.7 A More Detailed Investigation of Short-Range Ordering at the Interface

Interfacial properties are strongly tied to glass forming ability, ranging from the interfacial free energies role in controlling nucleation kinetics, to crystal surface properties such as the fill-factor and the nature and degree of ordering at the interface which strongly influences crystal growth-rates in the diffusion controlled regime. Tang and Harowell’s [45] molecular dynamics investigation of Cu_{50}Zr_{50}’s anomalously low unidirectional crystal growth-rates in comparison
to Ni$_{50}$Al$_{50}$ uncovered striking differences in the extent of chemical ordering present at the liquid-crystal interface. Large amplitude and long length-scale density correlations extending well into Ni-Al’s parent liquid phase were observed at the interface, while in contrast, correlations in the Cu-Zr parent phase rapidly decayed away from the boundary, with little indication of induced ordering beyond a few atomic layers. The extent of ordering at the interface was found to be highly dependent on the surface orientation for both systems, albeit, in a similar fashion [45].

While these considerations illustrate the importance of interfacial properties, a clear framework for explaining the above results is largely absent to this day. To certain degree, ordering at the interface can be seen to be controlled by the structure and orientation of the crystal itself, arising the possibility of fundamental limitations on compositional tuning methods strictly dependent upon properties of the disordered phase. Such limitations may be negligible should the susceptibility of ordering at the interface be primarily controlled by more fundamental properties regarding the disordered phase. It is therefore imperative to develop a clear understanding of what exactly governs the ordering susceptibility of the liquid phase when in contact with an arbitrary crystal surface. Based on the analysis of local structure/composition-energy correlations in the Cu-Zr and Ni-Al systems which were previously conducted in this study, bonding in the Ni-Al system was found to be significantly more geometrically and compositionally constrained, likely owing to its more short-ranged, covalent bonding character. Such bonding constraints are likely to preferentially favour low energy crystal compatible configurations. With this in mind, a possibility exists that these observed interfacial property differences are tied to these underlying bonding differences, and to the relative degree of short-ranged structural mismatch or similarity between the respective crystalline and disordered phases. More enhanced bonding constraints in the Ni-Al system towards lower local-energy configurations would impact the degree of structural mismatch allowed between neighbouring atoms at the crystal interface, thereby resulting in a slower decaying transition profile into the bulk liquid.

In order to investigating this further, liquid-crystal interfaces were generated following a similar approach as Tang and Harrowell [45]. The model generation procedure started with systems initialized according to the B2-crystal structure. Following an energy minimization stage, the middle one-third atoms were frozen/pinned, and systems were heated to temperatures well above the respective melting points (2300K for Ni-Al and 2100K for Cu-Zr) under zero pressure.
isobaric conditions, thereby melting unpinned atoms and forming two separate liquid-crystal interfaces. After a long equilibration stage, systems were subsequently cooled down to temperatures of interest for further property sampling. For both Ni-Al and Cu-Zr systems in question, both B2(100)-liquid and B2(110)-liquid interfaces were generated, with a sample snapshot of the Ni-Al B2(100) interface relaxed at 1900K presented in Figure 4.21.

![Figure 4.21: A molecular dynamics snapshot of the simulated Ni-Al B2(100) interface after relaxation at 1900K](image)

Preliminary results of this investigation have revealed subtle but potentially significant differences in local potential energy profiles away from Ni-Al and Cu-Zr interfaces. Viewing Figure 4.22 below, extracted Ni-Al/Cu-Zr density correlations and mean per-atom potential energy profiles as a function of distance away from the B2(100)-liquid interface is presented (at approximately equivalent superheated temperatures). Firstly, viewing the Cu and Zr density correlations, a clear mismatch is observed with Zr correlations being slightly shifted to further distances away from the interface. The reduced bond-strain and mismatch observed in the Ni-Al system is likely tied to previous observations of Ni-Al bond-length shortening and covalent character as seen in partial radial distribution function analysis of the Ni-Al system. Interestingly, even more dramatic mismatch is observed with respect to the relative positions of local energy minima of respective Cu and Zr energy profiles. Clear and well-defined energy minima consistent with density/distribution function profiles are observed in the Ni-Al system. In contrast, energy minima in the Cu-Zr system are much wider (less stiff), and in particular for Zr, display less correspondence with distribution function profiles. The less stiff and less defined local energy profiles may be reflective of the more metallic bonding character of the Cu-Zr
system, and in particular, greater short-range structural freedom. Future work is required to investigate short-range compositional ordering away from the interface, as well as a more in-depth analysis of underlying connections between short-range bonding constraints and disordered phase interfacial ordering susceptibilities.

**Figure 4.22:** Mean per-atom potential energies and chemical density distribution profiles away from the B2(110)-Crystal interface

### 4.4 Summary

Thermodynamic analysis of Ni-Al and Cu-Zr amorphous and B2 crystalline phases revealed lower phase stabilities for the Ni-Al system, most evident by Ni-Al’s larger free energy difference at $T_g$ and higher thermodynamic fragility. More significantly, the most marked indication of Ni-Al’s lower thermal stability was identified upon analysis of fractional liquid-crystal density differences in the two systems. Results for the Ni-Al system indicated fractional density differences ranging from $7 - 11\%$ along the quench, corresponding to values 2-3 times that of the Cu-Zr system. The $10\%$ volume change observed at $T_m$ in the Ni-Al system marks a significant departure from the $0 - 3\%$ volume change characteristic of good glass forming
systems. These results suggest an inherently kinetic origin to Ni-Al’s rapid crystallization rates. Surprisingly, the Ni-Al system was also identified to be the kinetically stronger system based on calculated strength and kinetic fragility parameters ($D^* = 2.07$ and 1.58, $m = 21.92$ and 25.01 respectively for Ni-Al and Cu-Zr), an unexpected result considering Ni-Al’s lower GFA and thermodynamic fragility. These anomalies were further elucidated upon by investigations of Gruneisen parameter, bulk stiffness, and structural relaxation properties in the two systems. Large Gruneisen parameters and a sudden spike in bulk stiffness properties were identified near 1.3$T_g$ in the Ni-Al amorphous phase, largely suggestive of the lower kinetic fragility being an artifact of underlying volume-strain and bond-stiffness dependencies. These findings provide detailed evidence that the poor efficacy of the kinetic fragility parameter as a GFA indicator in alloy systems containing metalloid species in general is largely connected with the short-range/covalent character of TM-M bonding and underlying anharmonicity effects.

Mismatch between underlying strain-stiffness dependencies of Ni-Al, Ni-Ni, and Al-Al partial bonds are likely an inhibiting force preventing bulk structural relaxation to globally efficient packing structures in the high temperature Ni-Al melt. Subsequently, the high temperature Ni-Al melt exhibits high free volume content and high diffusive and viscous transport rates. As the system is cooled, associated volume contraction results in significantly increased interactions among previously “non-bonded” or poorly bonded Ni-Al atoms, translating to a sudden spike in bulk stiffness properties (bulk moduli), viscosities, and ultimately to a lower kinetic fragility. In contrast, bonding in the Cu-Zr system is longer-ranged, less directional, and highly metallic in character, translating to minimal short-range bonding constraints, and promoting global structural relaxation (through more cooperative flow rearrangements) to lower free volume packing configurations. Structural evidence for the above included the more rapid decay density correlations extending from the nearest-neighbour to next-nearest-neighbour coordination shells in the Ni-Al system, most notably apparent upon comparison of the ratio of first and second peak heights (summarized in Table 4.4) for Ni-Al and Cu-Zr pair-correlation functions (3.05 and 2.50 respectively). In conjunction with these observations, the high first peak intensities and large extent of bond-length shortening observed suggest significantly more pronounced Ni-Al nearest-neighbour level interactions. In contrast, longer-ranged next-nearest-neighbour interactions appear much more pronounced in the Cu-Zr system, with strong and largely non-overlapping density correlations extending well into the 2nd, 3rd, and even 4th coordination shells indicative
of more pronounced long-range ordering. Furthermore, Voronoi analysis revealed higher icosahedral ordering in the Cu-Zr system (a signature of longer-ranged interactions and higher thermal stability of the amorphous phase) with higher fractions of $<0,0,12,0>$, $<0,2,8,2>$, and $<0,2,8,1>$ clusters, as well as the presence of significantly enhanced compositional short-range ordering. Analysis of chemical reordering along the quench was suggestive of the strong bond strain-stiffness dependencies previously identified in the Ni-Al system having the additional negative side-effect of inhibiting compositional short-range ordering in the amorphous phase, a likely contributing factor to Ni-Al’s lower GFA. The large atomic-mass mismatch between Ni and Al was further observed to result in significant mismatch in respective vibrational spectra, with Al partial frequency spectra extending to almost double the frequencies of Cu, Ni, or Zr. In contrast, Cu and Zr partial spectra were found to overlap with nearly identical profiles. These findings further illustrate the large extending impacts that simple bonding differences at the atomic level can have on a whole range of properties.

A comparative summary of GFA influencing factors evaluated for these two systems is presented in Appendix E. In addition, Appendix D tabulates the major influencing factors for GFA and their subsequent correlators.
Chapter 5

5 Development of a Broad-Compositional Search and Analysis Tool

The fine compositional sensitivity and the vast compositional space inherent to multi-component bulk metallic glassy systems makes the experimental compositional tuning and optimization of material properties a very taxing process, both in terms of labor and monetary costs. With the advent of large supercomputing facilities and advanced molecular dynamics techniques, computational materials engineering and discovery is becoming an ever more appealing and practical alternative (or supplement) to in-lab experimental materials exploration. In particular, the sampling of liquid, supercooled, and glassy phase (albeit, rapidly quenched) properties over vast temperature and compositional spaces with little to no prior knowledge of underlying systems is currently feasible utilizing molecular dynamics simulations techniques.

With this in mind, an automated and simple to use tool has been developed for the broad compositional surveying of material properties in binary, ternary, and quaternary alloy systems. PYTHON scripts have been developed which appropriately initialize LAMMPS input scripts and system configuration files for the simulated quenching and glass formation of metallic glasses based on user input information regarding the number of atoms, elemental base components, compositional ranges, sampling interval, and temperature domain to be explored. Respective simulations and property analysis scripts are automatically configured and organized into independent directories for each respective alloy composition. Provided access to supercomputing facilities, Bash job submission scripts (written for scheduling around the Cluster Resources Moab Workload Manager) have also been prepared which iteratively move through each compositional directory and submit requested jobs into the scheduling queue, allowing for the rapid processing of multi-composition, multi-temperature simulations in parallel.

Beyond automating the metallic glass model generation and simulation process, an array of PYTHON scripts have been prepared which process simulation output data for the external calculation of a large array of system properties, including the glass transition temperature, bulk moduli, pseudo-Gruneisen Parameters, thermodynamic properties, transport properties
(viscosities, diffusivities, and fragility), vibrational properties (vibrational density of states, vibrational entropy), and structural properties (total and partial radial distribution function and structure factors). C++ radical Voronoi tessellation packages (using the Voro++ library) in conjunction with PYTHON processing scripts have also been prepared, allowing for the automated collection of short-range cluster statistics and the analysis of structural reordering over the entirety of the quench domain. Extracted properties are output and saved into local files and directories in an easy to read and presentable text format, with key results plotted for quick viewing. In order to assess compositional trends and correlations between various properties of interest (potentially for compositional tuning applications), PYTHON scripts are further included which search through each individual compositional directory and extract relevant property results. These results are output and automatically plotted for viewing purposes. Post-analysis scripts described were all written in a modular format, making any future required modifications simple and straightforward. More detailed instructions for the use of this toolkit are available in the provided user manual.

5.1 A Broad-Compositional Investigation of Short-range Ordering, Fragility, and Glass Forming Ability in the Cu-Zr System

In the following sections of this chapter, results of a broad-compositional investigation into the kinetic, and structural properties of the Cu$_x$Zr$_{(100-x)}$ alloy system over a range of 35-85% Cu sampled at 5% composition intervals is presented. Due to the strong correlations between polytetrahedral and compositional short-range ordering, the fragility parameter, and glass forming ability, a combined analysis of their broad compositional variations in the Cu-Zr system is of interest. For all compositions simulated, bulk liquid and glassy phases were generated by first heating randomly ordered systems of 6000 atoms from 300K to 2100K over a duration of 1000ps, followed by a 2000ps relaxation stage allowing for the proper equilibration of the high temperature liquid melt. Following equilibration, systems were subsequently cooled down to a temperature of 100K through a series of 25K quench(100ps) and hold(200ps) stages, corresponding to an average linear cooling rate of ~0.1K/ps. Throughout the quenching process, zero pressure isobaric conditions were applied using NPT Nose-Hoover temperature and pressure controls under 2fs integration time-steps. In contrast to Chapter 2, however, the 2007 Cu-Zr
Mendelev [58] interatomic potential was used for simulations in this section due to the broader range of compositional data used in its functional fitting during development.

5.1.1 Transport and Kinetic Properties

Melt viscosities were assessed over a temperature range of 1.2-1.8T_g in 50K intervals for each simulated Cu-Zr composition. In order to quantitatively assess kinetic fragilities in each system, viscosity data were fit to the Vogel-Fulcher-Tammann (VFT) form:

\[
\eta(T) = \eta_0 \exp\left(\frac{D^*T_0}{T - T_0}\right)
\]

Where \(\eta_0\) is the high temperature viscosity limit, \(T_0\) is the divergence temperature (often close in value to the Kauzmann temperature \(T_K\)), and \(D^*\) is the strength parameter. Kinetic fragility parameters (3.17) were further estimated by interpolating viscosities down to a rheological glass transition temperature \(T_g\) identified by the rheological condition that \(\eta(T_g) = 10^3 \text{Pa} \cdot \text{s}\) (see “Transport Property and Fragility Calculations” in methodology and computational details for a detailed discussion of the physical basis for using this alternative viscosity condition instead of the standard rheological condition of \(\eta(T_g) = 10^{12} \text{Pa} \cdot \text{s}\) which applies under experimental conditions). Specifically relevant to glass forming ability are strength parameter, \(D^*\), fragility parameter, \(m\), and effective activation energy parameter, \(B = D^*/T_0\), which are all reflective of overall transport properties in the supercooled domain, and possess significant correlation with glass forming ability. Compositional trends for these parameters, in conjunction with extracted glass transition temperatures from cooling curve data are plotted below in Figure 5.1.

Viewing the results, significant compositional sensitivity is apparent for all three kinetic parameters of interest. Considering that larger \(D^*\) parameters and smaller kinetic fragility parameters \(m\) are positively correlated with GFA, the compositional trends observed about 50% and 65% Cu content are indicative of high glass forming ability. Interestingly, clear correspondence between these preliminary results based on kinetics alone with two out of three of the best identified GFA compositions [29] in the Cu-Zr system of Cu_{64}Zr_{36}, Cu_{56}Zr_{44}, and Cu_{50}Zr_{50} is evident. Surprisingly, however, the Cu_{50}Zr_{50} system is substantially less fragile relative to Cu_{65}Zr_{35}, while the glass forming ability of the two systems in practice is fairly
similar (critical thicknesses of glass formation determined by Li et al. [29] are about 1.15mm, 1.00, and 1.15mm for Cu$_{64}$Zr$_{36}$, Cu$_{56}$Zr$_{44}$, and Cu$_{50}$Zr$_{50}$ respectively).

**Figure 5.1:** Compositional dependencies of the glass transition temperature and key kinetic properties

5.1.2 Chemical and Topological Short-Range Ordering

Atomic nearest-neighbour information extracted from Voronoi tessellation were utilized for the investigation of local compositional ordering through calculation of the Warren-Cowley Parameter. Denoting $<\text{CN}>$ as the mean total coordination number (or mean number of nearest-nearest neighbours), $<\text{CN}_{ij}>$ the mean coordination of species j atoms about species i central atoms, and $c_i$ the bulk stoichiometric concentration of species i, the Warren-Cowley parameter $\alpha_p$ is calculated through the following relation:
\[ \alpha_p = \frac{c_i < CN -< CN_{ij} >}{c_i < CN >} = \frac{c_j < CN -< CN_{ij} >}{c_j < CN >} \]  

(3.21)

viewing the relation above, the Warren-Cowley parameter serves to quantify the average deviation of local compositions (comprised of atoms in the first coordination shell) from that of the bulk (stoichiometric composition) in a normalized fashion. Greater local compositional deviations from bulk stoichiometry are a signature of enhanced compositional short-range ordering (CSRO) in the amorphous phase.

In addition, copper, zirconium, and total system polyhedra fractions for perfect icosahedral clusters \(<0,0,12,0>\) (also equivalent to the CN=12 Kasper polyhedra), the coordination 16 Kasper polyhedra \(<0,0,12,4>\), and geometrically unfavorable motifs (GUMs) identified by Ding et al. [56] as active localized fluid domains in the Cu_{64}Zr_{36} system were further calculated along the quench. Results of this analysis at reference temperature \(T_g\) are plotted below in Figure 5.2.

**Figure 5.2:** Compositional Dependencies of chemical short-range ordering and fractions of key polyhedral types
Viewing the results of the short-range topological and compositional ordering analysis presented in the figure below, enhanced CSRO is apparent for the Cu$_{50}$Zr$_{50}$ (corresponding to a clear minima in the Warren-Cowley parameter), while in contrast, the Cu$_{65}$Zr$_{35}$ composition is observed to exhibit optimal icosahedral fractions. Little notable features are apparent about the Cu$_{55}$Zr$_{45}$ composition with regards to CSRO or icosahedral ordering. Interestingly, the Cu$_{50}$Zr$_{50}$ which was previously identified to possess the lowest fragility out of the three compositions also exhibits the largest extent of compositional short-range ordering, while simultaneously possessing maximum GUM fractions. On the other extreme, the Cu$_{65}$Zr$_{35}$ appears to exhibit the least degree of compositional short-range ordering (with near Warren-Cowley parameters closest to zero), while simultaneously appearing to possess the highest degree of short-range icosahedral ordering with high fractions of perfect icosahedra ($<0,0,12,0>$) for Copper central atoms, and Kasper CN=16 polyhedra ($<0,0,12,4>$) for Zirconium central atoms. These result therefore appear to indicate that a higher degree of polytetrahedral ordering in the Cu$_{65}$Zr$_{35}$ counter-acts the higher underlying fragility relative to Cu$_{50}$Zr$_{50}$ (despite also possessing lesser CSRO), resulting in nearly identical glass forming abilities in the two systems.

5.1.3 Summary

The successful prediction of the two highest GFA compositions Cu$_{50}$Zr$_{50}$, and Cu$_{64}$Zr$_{36}$ through purely kinetic and structural considerations of the disordered phase supports the concept of developing a liquid-only MD-based compositional tuning approach. The general absence of any interesting or anomalous features (maxima/minima) in any singular predictive indicator near the third best GFA composition, Cu$_{56}$Zr$_{44}$, suggests that its high GFA may be attributed to a more complex combination of effects or due to other variables unaccounted for in this study. The development of a combined performance index incorporating all of these factors may be a potential solution for the prediction of high GFA alloys in such situations. Additional sampling points about the Cu$_{50}$Zr$_{50}$ compositional domain are needed however in order to more conclusively substantiate these notions. With the Li et al [29] analysis of fractional density changes upon crystallization indicating low extents of free volume in the Cu$_{56}$Zr$_{44}$, however, these findings further enforce the notion that the extent of free volume in the disordered phase is the single best predictive indicator for glass forming ability.
Chapter 6

6 Conclusions and Future Work

The computational search and discovery of high GFA alloys is currently limited to the use of GFA indicators which neglect to account for underlying differences in bonding properties or even the alloy class in question. After conducting a thorough analysis of GFA influencing factors and predictive indicators (see Appendix D), Ni-Al and Cu-Zr metallic glasses were simulated using molecular dynamics techniques with the overall aim of investigating underlying connections to more fundamental properties at the atomic level. The efficacies of various predictive indicators of GFA were assessed through direct computation (see Table E.1 in Appendix E for a summary of these results), and in cases of their subsequent failures to infer GFA, detailed investigations of bulk and atomic-level properties were conducted with the intent of uncovering underlying causes. Utilizing knowledge and tools developed during this work, an automated MD-based package was created for the broad-compositional surveying and analysis of amorphous phase properties relevant to GFA in multicomponent alloy systems. Broad compositional sampling and analysis of kinetic and structural properties in the Cu-Zr system was subsequently conducted. Reflecting upon the original aims of this work:

1) Explore and identify the key influencing factors and predictive indicators of glass forming ability in multicomponent alloy systems
   o Status: Complete

2) Investigate the atomic-level influencing factors of glass forming ability in Cu-Zr and Ni-Al metallic glasses
   o Status: Complete

3) Investigate compositional dependencies of short-range ordering, transport properties, and glass forming ability in the Cu-Zr system
   o Status: Complete

4) Develop an automated computational tool for the broad-compositional search and analysis of thermodynamic, kinetic, and structural properties in multicomponent glasses
   o Status: Complete
6.1 Summary and Main Contributions

In Chapters 2 and 3, a detailed review of the supercooling process underlying glass formation, the fundamental influencing factors governing crystallization kinetics, the key predictive indicators of glass forming ability in multicomponent alloys, and lastly, the methodology underlying simulation and property extraction techniques used for their subsequent investigation in this study were presented. With crystal nucleation and growth kinetics tending to be severely diffusion limited processes in high GFA alloys, the key predictive indicators of GFA are identified to be high disordered (liquid and glassy) phase packing efficiency, low melt fragility and overall transport properties throughout the supercooled domain, enhanced dynamic decoupling between the atomic mobilities of constituent elemental species (and a greater extent of Stoke-Einstein breakdown), enhanced compositional short-range order and complexity in the disordered (and crystal phase), and enhanced short-range icosahedral and polytetrahedral (close-packed) order. Considering that all of these properties are intrinsically associated with the disordered phase, the prospect of a rapid and robust compositional tuning approach reliant upon disordered phase properties alone is deemed to be possible.

Underlying differences in the nature of atomic level bonding are reflected through more general differences in the degree and nature of short and medium-range ordering, energy landscape and structural relaxation properties, and ultimately the mechanisms through which crystal nucleation and growth occur. Consistent with these notions is the rapid crystal nucleation and growth rates observed in the Ni\textsubscript{50}Al\textsubscript{50} system in comparison to Cu\textsubscript{50}Zr\textsubscript{50}, an apparently anomalous result which largely persists to be a source of confusion in the BMG community. Investigations of thermodynamic, kinetic, and structural properties in the equimolar Ni-Al and Cu-Zr systems conducted in Chapter 4 of this work revealed a number of fundamental differences in the nature of bonding and interactions in respective amorphous phases. The short-range directional bonding and reduced atomic size mismatch (due to the significant bond-length shortening) between constituent Ni and Al elements in the Ni-Al system lead to less chemically preferential short-range ordering, a reduced tendency towards high coordination and topologically close packed icosahedral short-range clusters, increased bulk structural stability with respect to local defects in the crystal phase and to free volume in the disordered phase (due to less medium-range connectivity and reduced collective flow behavior associated with the stiffer and more constrained/directional short-ranged bonding) and a subsequently increased stability of the
crystallizing phase to local compositional variations and the formation of a less chemically constrained solid-solution. These factors all contribute toward the destabilization of the Ni-Al supercooled melt, resulting in a high free volume, thermodynamically unstable disordered phase with a highly interface-controlled crystallization pathway possessing minimal short-range or long-range diffusion kinetic limitations. Large atomic-mass differences lead to significantly higher vibrational frequencies for lighter Al atoms when bonded to heavier Ni atoms, and increased overall atomic vibrational mismatch and variability in the disordered phase. This vibrational mismatch and variability, in conjunction with enhanced anharmonicity and strain-stiffness dependencies associated with the short-range covalent character of Ni-Al bonding lead to significant structural relaxation and transport property dependencies on temperature and chemical reordering in the undercooled melt domain. The anomalously low melt fragility of the Ni-Al system can therefore be seen to be an artifact of these underlying dependencies.

Lastly, as a first step in the development of a “liquid-only” simulations-based GFA tuning approach, an automated tool has been created for the broad compositional sampling and analysis of liquid and glassy phase properties in multicomponent (binary, ternary, quarternary) alloy systems, with initial work on the Cu-Zr system presented in Chapter 5 showing very promising results. The successful prediction of the two highest GFA compositions, Cu$_{50}$Zr$_{50}$ and Cu$_{64}$Zr$_{36}$, through purely kinetic (melt fragility) and short-range chemi-topological (icosahedral fractions and CSRO) considerations of the disordered phase further supports the viability of a liquid-only MD-based compositional tuning method. The next step in the development of such an approach is the incorporation of other disordered phase predictive GFA indicators, and subsequent testing on ternary or quarternary alloy systems. The overall findings of the Ni-Al and Cu-Zr GFA investigations, however, demonstrate the critical importance of incorporating more complex alloy-specific information regarding the nature of bonding and ordering at the atomic level into such an approach.
6.2 Implications of Results and Future Avenues of Research

Implications of this work relevant to the advancement of compositional tuning methods, and potential future avenues of research are:

- Traditional free volume frameworks for diffusive motion and transport are likely to break down in alloys containing high concentrations of metalloid species due to the short-ranged/directional covalent character of TM-M bonding

- The poor efficacy of the fragility index as a GFA indicator in TM-M alloy systems is likely tied to underlying vibrational an-harmonicity effects and bond strain-stiffness dependencies associated with the mismatch between short-ranged/covalent TM-M bonding, and longer-ranged/metallic TM-TM bonding

- The atomic mass-ratio may be an important parameter of interest independent of the atomic size-ratio, with key connections to underlying vibrational mismatch between constituent elements, the melt fragility, and subsequently, the overall GFA

- Base BMG components should ideally be larger metallic species so as to ensure longer-ranged interactions and lesser nearest-neighbour bonding constraints, which together contribute to enhance medium-range chemical ordering, connectivity, and collective flow behavior, as well as driving the formation of more topologically close packed, icosahedral short-range order in the disordered phase

- Liquid-crystal density difference is the single most effective GFA indicator, however, proposed free volume theory based explanations provide at most a partial explanation for said efficacies. It is likely that in systems containing high fractions of metalloid species, a complete explanation requires consideration of induced stress fields at the liquid-crystal interface tied to underlying liquid-crystal density differences, bond an-harmonicity effects in the amorphous phase, and higher stiffness properties of the crystalline phase.

- A potential avenue for future research is the modification of common GFA indicators such as the fragility index to account for underlying bonding and vibrational property differences, potentially through the addition of terms accounting for an-harmonicity and bonding/mass mismatch. In conjunction, cross-compositional analysis of (pseudo)Gruneisen parameters along the quenching domain may be worthwhile for the search of improved GFA indicators.
Bibliography


Appendix A. Background Information on Classical Equilibrium Statistical Mechanics

Classically, the state of a physical system can be fully described given complete knowledge of atomic/particle positions, \( \mathbf{r}^{(N)} = (\mathbf{r}_1, \mathbf{r}_2, \ldots , \mathbf{r}_N) \), and momenta, \( \mathbf{p}^{(N)} = (\mathbf{p}_1, \mathbf{p}_2, \ldots , \mathbf{p}_N) \), (often further condensed into a single 6N dimensional phase space coordinate, \( \mathbf{x}^{(6N)} = (\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) \), with evolution following under the relations of Hamiltonian/Newtonian mechanics. Within this context, the system energy (or Hamiltonian function) can be decomposed into components of either kinetic or potential energy, for which the potential energy is often taken to be only a function of the relative atomic positions:

\[
H(\mathbf{x}^{(N)}) = KE + PE = \sum \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} + \phi(\mathbf{r}^{(N)})
\]  
(A.1)

\[
\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i}
\]

\[
\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} = -\frac{\partial \phi(\mathbf{r}^{(N)})}{\partial \mathbf{r}_i}
\]

In practice, exact knowledge of the microscopic state of a physical system is never known (nor possible to be known), with available information often limited to coarse-grained bulk-averaged observables (i.e. density, net magnetism, phase, etc.). With this in mind, at the heart of equilibrium statistical mechanics is the goal of predicting and understanding thermodynamic properties of bulk physical systems through the probabilistic consideration of the underlying microscopic state space (configurations) and energetics. In essence, this is done by averaging system observable properties \( B(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) \) over a representative distribution in phase space \( f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) \) which is appropriately weighted to quantify the probability of the system occupying different configurational volumes, i.e.:

\[
\text{Probability of sampling microstate in ensemble with coordinates in range } (\mathbf{r}^{(N)}, \mathbf{r}^{(N)} + d\mathbf{r}^{(N)}) \text{ and } (\mathbf{p}^{(N)}, \mathbf{p}^{(N)} + d\mathbf{p}^{(N)}) \text{ at time } t = \int f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}
\]  
(A.2)
With the expectation value of macroscopic observables (at a given instance in time) corresponding to an ensemble average over all accessible phase space:

$$\overline{B(t)} = \int d\mathbf{r}(N) \, d\mathbf{p}(N) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) B(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$$  (A.3)

The key problem is then transferred to the identification of the appropriate distribution function for weighting different configurations. Under the framework of equilibrium statistical mechanics, a constrained maximum entropy axiomatic approach is taken, with the key caveat being the requirement for the conditions of ergodicity, stationarity, and subsequently equilibrium to be met. The requirement of stationarity imposes time translational invariance to the distribution function with the additional requirement for ergodicity imposing equal weighting to all accessible microstates of identical number of particles, volume, and energy, resulting in the constant weight microcanonical NVE ensemble (distribution function):

$$f(\mathbf{x}^{(N)}) = \begin{cases} 
\frac{1}{\Omega(N, V, E)} & \text{if } E < H(\mathbf{x}^{(N)}) < E + \delta E \\
0 & \text{else}
\end{cases}$$  (A.4)

An additional consequence of the ergodic hypothesis is the equivalence of time and ensemble averaging, with the expected duration of time spent by a system in a region of accessible phase space being directly proportional to the associated volume of that region.

$$\overline{B(t)} = \frac{1}{\tau} \int_0^\tau B(\mathbf{r}^{(N)}(t + \epsilon), \mathbf{p}^{(N)}(t + \epsilon)) d\epsilon \approx \frac{1}{\Omega(N, V, E)} \int d\mathbf{r}(N) d\mathbf{p}(N) B(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = < B >$$  (A.5)

Informally speaking, this axiomatic approach assumes that measurement timescale is long enough (in comparison to underlying relaxation processes) to allow for sufficient sampling of phase space. The observed macroscopic properties of an isolated system are then seen to correspond to the macroscopic state associated with the greatest number of accessible microstates, and thus, that which is the most “disordered” or possesses maximal entropy. By defining the statistical entropy as the logarithm of the total number of independent microstates ($\Omega$ or multiplicity) accessible at that given volume, particle number, and total energy, the connection between the statistical and thermodynamic entropy $S$ is realized through the relations:
\[ S = k_B \ln \Omega(N,V,E) \] where \( k_B \) is the Boltzmann Constant \( (A.6) \)

\[ \Omega(N,V,E) = \frac{1}{N! h^3 N} \int_{E<H(x^{(N)})<E+\delta E} \exp\{-\beta H(x^{(N)})\} \, d\mathbf{x}^{(N)} d\mathbf{p}^{(N)} \]

(Note: the \( \frac{1}{N! h^3 N} \) pre-factor and integration over states existing within a finite energy band \( \delta E \) is required for consistency with quantum statistics and uncertainty)

While no mention has been made till now with respect to system boundary conditions or the degree/nature of coupling with the surroundings, such considerations can be incorporated as additional optimization constraints for the determination of the appropriate distribution function, forming the basis for the various thermodynamic ensembles (microcanonical/NVE, canonical/NVT, grand-canonical/\( \mu \)VT, isothermal-isobaric/NPT and so on). While the microcanonical ensemble formed under the assumption of complete isolation (with constant energy, volume, and particle number) is the most fundamental, a significant disadvantage lies in the fact that experiments are rarely conducted under such operating conditions. Relaxing constraints from the condition of constant energy to constant temperature instead is much more reflective of commonly encountered experimental conditions. In such instances, it can be shown that the canonical (NVT) ensemble is the appropriate distribution function, with occupation probabilities weighted exponentially according to system energy \( H(x^{(N)}) \):

\[ f(x^{(N)}) = \frac{1}{N! h^3 N} \frac{\exp\{-\beta H(x^{(N)})\}}{Z(N,V,T)} \] \( (A.7) \)

where \( \beta = \frac{1}{k_B T} \) denotes the inverse temperature, \( Z(N,V,T) \), is the Canonical Partition Function.

Beyond ensuring proper normalization, the Canonical Partition Function contains all information of the system, and can be seen to provide a direct connection to the thermodynamic state function Helmoltz Free Energy (A):

\[ Z(N,V,T) = \frac{1}{N! h^3 N} \int dx^{(N)} \exp\{-\beta H(x^{(N)})\} \]

\[ A = \bar{E} - TS = -\beta^{-1} \ln(Z(N,V,T)) \]
Importantly, macroscopic thermodynamic observables are directly relatable to the partition function. For instance, evaluation of the mean system energy, \( \bar{E} \), through explicit ensemble averaging of the system Hamiltonian, \( H(x^{(N)}) \), reveals its connection to the partition function as a first order partial derivative with respect to \( \beta \):

\[
\bar{E} = \langle H(x^{(N)}) \rangle = \frac{1}{N! h^{3N}} \int dx^{(N)} \exp\{-\beta H(x^{(N)})\} H(x^{(N)}) = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial (\beta A)}{\partial \beta} \tag{A.9}
\]

Moreover, energy fluctuations/variance for systems operating under NVT conditions can explicitly be evaluated in terms of a second order partial derivative of the partition function and shown to be directly related to the constant volume heat capacity, \( C_v \):

\[
\sigma_E^2 = \langle (H(x^{(N)})^2) \rangle - \langle H(x^{(N)}) \rangle^2 = -\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{\partial \bar{E}}{\partial \beta} = k_B T^2 C_v \tag{A.10}
\]

As presented in Section 3.3, similar statistical identities can be derived relating other second order thermodynamic properties to fluctuations in corresponding first order thermodynamic properties, forming the basis for the fluctuation method used in this work for the extraction of heat capacities, isothermal expansion coefficients, and bulk moduli through MD simulation.

Thermodynamic stability and more fundamental questions regarding the connection between statistical mechanics and classical thermodynamics can be further elucidated by analyzing the associated probability of sampling a macroscopic state of total energy, \( E_1 \), from a system operating under NVT conditions:

\[
P(E_1) = \langle \delta(E_1 - H(x^{(N)})) \rangle_{NVT} \tag{A.11}
\]

\[
= \frac{1}{N! h^{3N} Z(N, V, T)} \int dx^{(N)} \exp\{-\beta H(x^{(N)})\} \delta(E_1 - H(x^{(N)}))
\]

\[
= \frac{\exp\{-\beta E_1\} \Omega(E_1)}{Z(NVT)}
\]

From (A.6), the multiplicity of states of energy \( E_1 \), \( \Omega(E_1) \), can be expressed in terms of the corresponding entropy, \( S(E_1) \), resulting in:
\[
\begin{align*}
P(E_1) & \sim \exp \left\{ -\frac{E_1}{k_B T} \right\} \exp \left\{ \frac{S(E_1)}{k_B} \right\} \\
& = \exp \left\{ -\frac{E_1 - TS(E_1)}{k_BT} \right\} \\
& = \exp \left\{ -\frac{A(E_1)}{k_BT} \right\}
\end{align*}
\] (A.12)

We see that the probability of capturing the system in a state of energy, \(E_1\), is directly related to the corresponding Helmholtz Free Energy, \(A(E_1) = E_1 - TS(E_1)\), with lower Helmholtz Free Energies translating to higher occupation probabilities and thermal stability. The relative stability of the energy macrostate, \(E_1\), with respect to \(E_2\), can similarly be expressed in terms of the Helmholtz Energy difference, \(\Delta A_{12} = A(E_1) - A(E_2)\):

\[
\begin{align*}
\frac{P(E_1)}{P(E_2)} &= \exp \left\{ -\frac{E_1 - TS(E_1)}{k_BT} \right\} \exp \left\{ -\frac{E_2 - TS(E_2)}{k_BT} \right\} = \exp \left\{ -\frac{\Delta E_{12} - T\Delta S_{12}}{k_BT} \right\} = \exp \left\{ -\frac{\Delta A_{12}}{k_BT} \right\}
\end{align*}
\] (A.13)

While the above discussion is restricted to the use of total energy \(E\) as the thermodynamic observable property for characterizing different macrostates, the main results apply in general. Namely, the identification of the most thermodynamically stable (equilibrium) state/phase of a system can be equivalently framed in terms of probability maximization under the ensemble distribution, or alternatively, one of free energy minimization. From this perspective, the standard thermodynamic condition for process spontaneity (\(\Delta A_{1\rightarrow 2} < 0\)) under NVT operating conditions can be viewed to be a simple statement that spontaneous processes evolve toward more probabilistically favourable, lower free energy states. Furthermore, the equilibria of two distinct states or phases can be interpreted in terms of the condition of equal system occupational probabilities or Free Energies. Under different operating conditions, the identification of the most thermodynamically stable state/phase can similarly be framed in terms of probability maximization, or alternatively, in terms of Entropy (S) maximization under NVE conditions, Gibbs free energy (G) minimization under NPT/ \(\mu\)VT conditions, or even in terms of internal energy (E) minimization under NVS isentropic conditions. Viewing Table A.1, distribution
functions, partition functions, and associated thermodynamic potentials (or state functions) for systems operating under various standard conditions are summarized.

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Distribution Function</th>
<th>Partition Function</th>
<th>Thermodynamic Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcanonical (NVE)</td>
<td>( f(x^{(N)}) = \begin{cases} \frac{1}{\Omega(N,V,E)} &amp; \text{if } H(x^{(N)}) = E \ 0 &amp; \text{else} \end{cases} )</td>
<td>( \Omega(N,V,E) = \frac{1}{N!} \int_{H(x^{(N)})=E} \Omega(x^{(N)}) , dx^{(N)} )</td>
<td>( S(N,V,E) = k_B \ln\Omega(N,V,E) )</td>
</tr>
<tr>
<td>Canonical (NVT)</td>
<td>( f(x^{(N)}) = \frac{1}{N!h^{3N}} \exp{-\beta(H(x^{(N)}) - PV)} ) ( \frac{1}{Z(N,V,T)} )</td>
<td>( Z(N,V,T) = \frac{1}{N!h^{3N}} \int dx^{(N)} \exp{-\beta(H(x^{(N)}) - PV)} )</td>
<td>( A(N,V,T) = -k_B T \ln \Omega(N,V,T) ) ( A(N,V,T) = E_{\text{ideal}} - TS )</td>
</tr>
<tr>
<td>Isothermal-Isobaric (NPT)</td>
<td>( f(x^{(N)} , V) = \frac{1}{N!h^{3N}} \exp{-\beta(H(x^{(N)}) + PV)} ) ( \frac{1}{\Delta(N,P,T)} )</td>
<td>( \Delta(N,P,T) = \int_{V=0}^{\infty} dV Z(N,V,T) \exp{-\beta PV} )</td>
<td>( G(N,P,T) = -k_B T \ln \Omega(N,P,T) ) ( G(N,P,T) = \mu N + E_{\text{ideal}} - TS + PV )</td>
</tr>
<tr>
<td>Grand Canonical ((\mu)VT)</td>
<td>( f(x^{(N)} , \mu) = \frac{1}{N!h^{3N}} \exp{-\beta(H(x^{(N)}) + \mu N)} ) ( \Xi(\mu,V,T) )</td>
<td>( \Xi(\mu,V,T) = \sum_{N=0}^{\infty} Z(N,V,T) \exp{(\beta \mu N) } )</td>
<td>( G(\mu,V,T) = -k_B T \ln \Xi(\mu,V,T) ) ( G(\mu,V,T) = \mu N + E_{\text{ideal}} - TS + PV )</td>
</tr>
</tbody>
</table>
Appendix B. An In-Depth Overview of Energy Landscape Theory

Under the energy landscape formulism [13-15], the 3N dimensional potential energy landscape \( \phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N) \) is partitioned about a discrete set of configurations, \( \{\mathbf{r}_a^{(N)}\} \), known as “basins” or “inherent structures” where the potential energy lies at a local minima with respect to all atomic coordinates (and thus is in a state of local dynamical equilibrium, experiencing zero force). Within this context, system dynamics and evolution in the supercooled domain can be characterized by the combined contributions of an-harmonic intra-basin vibrations about local potential energy (basin) minima, and more larger-scale and in-frequent “basin hopping” transitions across potential energy saddle-points to nearby thermally accessible basins. In order to understand the basis of such configurational partitioning, first recall that the canonical partition function is expressed as a 6N-dimensional integral over configurational and momenta space (while NVT operating condition are assumed here for brevity, the same overall results apply under the isothermal-isobaric NPT ensemble where partitioning occurs in the 3N+1 dimensional (zero temperature) enthalpy landscape instead of the 3N dimensional potential energy landscape [48]):

\[
Z(N, V, T) = \frac{1}{N! h^{3N}} \int d\mathbf{x}^{(N)} \exp\left\{ -\beta H(\mathbf{x}^{(N)}) \right\} \\
= \frac{1}{N! h^{3N}} \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \exp\left\{ -\beta \left( \sum \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} + \phi(\mathbf{r}^{(N)}) \right) \right\} \\
= \frac{1}{N! h^{3N}} \int d\mathbf{p}^{(N)} \exp\left\{ -\beta \sum \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} \right\} \int d\mathbf{r}^{(N)} \exp\left\{ -\beta \phi(\mathbf{r}^{(N)}) \right\}
\]

The separable nature of the Hamiltonian into kinetic and potential energy components allows for momenta contributions to be evaluated independently, amounting to standard Gaussian integrals (from \(-\infty\) to \(+\infty\)) which can be calculated explicitly and shown to be given by:

\[
\int d\mathbf{p}^{(N)} \exp\left\{ -\beta \sum \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} \right\} = (2\pi m_B T)^{3N/2}
\]
The Configurational Partition Function, \( Q(N, V, T) \), containing all interaction and configurational energy influences can therefore be defined as:

\[
Q(T, V) = \int d\mathbf{r}^{(N)} \exp\{-\beta \phi(\mathbf{r}^{(N)})\}
\]

(B.3)

Defining the thermal De-broglie wavelength, \( \lambda_D \):

\[
\lambda_D = \left( \frac{h^2}{2\pi mkT} \right)^{\frac{1}{2}}
\]

(B.4)

the decomposition of the full Partition Function in terms of the configurational partition function can be simply expressed as:

\[
Z(N, T, V) = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}} Q(T, V) = \frac{1}{N! \lambda_D^{3N}} Q(T, V)
\]

(B.5)

As stated earlier, the partition function can further be partitioned in configurational space about a discrete set of potential energy minima. Conceptually, this can be understood by considering classical system evolution following under Hamiltonian/Newtonian dynamics which is governed by:

\[
\ddot{\mathbf{r}}^{(N)} = \nabla_{\mathbf{r}^{(N)}} \phi(\mathbf{r}^{(N)})
\]

(B.6)

By neglecting dynamics and only considering the first-order evolution equations, steepest decent paths are characterized by:

\[
\dot{\mathbf{r}}^{(N)} = \nabla_{\mathbf{r}^{(N)}} \phi(\mathbf{r}^{(N)})
\]

(B.7)

It can be shown [13-15] that following the governing first-order steepest decent path, any point in configurational space (with the exception of a discrete volume of zero measure) maps to a corresponding local minimum in the discrete set of \( \{ \mathbf{r}_\alpha^{(N)} \} \). All elements of configurational space mapping to minima \( \mathbf{r}_\alpha \) define sub-regions, \( R(\mathbf{r}_\alpha^{(N)}) \), known as the "quench regions", "basins", or "inherent structures". The configuration integral can thus be expressed as a sum over the individual quench regions or basins:
\[
Q(T,V) = \sum_{\alpha} Q_{\alpha} = \sum_{\alpha} \int_{R(r_{\alpha}^{(N)})} d r^{(N)} \exp\{-\beta \phi(r^{(N)})\} \tag{B.8}
\]

Where \( Q_{\alpha} \) is the Configurational Partition function for the individual and distinct basin, \( R(r_{\alpha}^{(N)}) \).

Expressing the Potential energy, \( \phi(r^{(N)}) \), in terms of its difference with respect to the local minima energy at \( r_{\alpha}^{(N)} \), \( \Delta_{r_{\alpha}^{(N)}} \phi(r^{(N)}) \), thermal/vibrational contributions can be effectively separated, allowing \( Q_{\alpha} \) to be expressed as:

\[
Q_{\alpha}(T,V) = \exp\{-\beta \phi(r_{\alpha}^{(N)})\} \int_{R(r_{\alpha}^{(N)})} d r^{(N)} \exp\{-\beta \Delta_{r_{\alpha}^{(N)}} \phi(r^{(N)})\} \tag{B.9}
\]

Averaging over all basins of equivalent inherent structure (minima) energies, one can define the mean partition coefficient, \( Q(\phi,T,V) \), and mean vibrational free energy, \( f(\phi,T,V) \), for inherent structures of energy \( \phi \):

\[
Q(\phi,T,V) = \frac{\sum_{\alpha} \delta_{\phi,\phi_{\alpha}} Q_{\alpha}}{\sum_{\alpha} \delta_{\phi,\phi_{\alpha}}} = \exp\{-\beta \phi\} < \int_{R(\phi)} d r^{(N)} \exp\{-\beta \Delta_{r_{\alpha}} \phi(r^{(N)})\} > \tag{B.10}
\]

\[
f(\phi,T,V) \equiv -\beta^{-1} \ln \frac{< \int_{R(\phi' IS)} d r^{(N)} \exp\{-\beta \Delta_{r_{\alpha}} \phi(r^{(N)})\} >}{\lambda^{3N}} \tag{B.11}
\]

\( f(\phi,T,V) \) can be interpreted as the (vibrational) free energy should the system be completely confined to the average inherent structure of depth \( \phi \). The number of distinct basins of potential energy \( \phi \), \( \Omega(\phi) \), is further given by:

\[
\Omega(\phi) = \sum_{\alpha} \delta_{\phi,\phi_{\alpha}} \tag{B.12}
\]

Coarse graining \( \Omega(\phi) \), a density of states, \( N(\phi) \), can be defined as:

\[
N(\phi) \delta \phi = \int_{\phi}^{\phi + \delta \phi} d \phi' \Omega(\phi') \approx \Omega(\phi) \delta \phi \tag{B.13}
\]
and the configurational entropy, \( S_c \), can be defined as:

\[
S_c(\phi) = k_B \ln[\Omega(\phi)\delta\phi]
\]  

(B.14)

Denoting the lowest potential energy (crystalline state), \( \phi_o \), and the highest energy stable packing state, \( \phi_u \), it is apparent that basin energies associated with all other stable packings lie somewhere in the range of \( \phi_o \leq \phi \leq \phi_u \). The Configurational Partition function can thus be expressed as an integral over inherent structure energies:

\[
Q(T, V) = \int_{\phi_o}^{\phi_u} d\phi \Omega(\phi)Q(\phi, T, V)
\]

(B.15)

with the full Partition Function therefore being expressed as:

\[
Z(N, T, V) = \frac{1}{N! \lambda^N} \int_{\phi_o}^{\phi_u} d\phi \exp\{-\beta S_c(\phi)T + \phi + f(\phi, T, V)\}
\]

(B.16)

and resulting in the probability of quenching to an inherent structure of energy, \( \phi \), at temperature, \( T \):

\[
P(\phi, T, V) = \frac{\exp\{-\beta S_c(\phi)T + \phi + f(\phi, T, V)\}}{Z(N, T, V)}
\]

(B.17)

As usual, the Helmholtz Free Energy, \( A \), is given by:

\[
A(N, T, V) = -kT \ln Z(N, T, V)
\]

(B.18)

In the thermodynamic limit where \( N \rightarrow \infty \), this can be approximated to first order by taking a maximum integrand approach [13-15], resulting in the final expression for the system free energy:
\[ A(T, V) \approx \phi - T S_c(\phi) + f(\phi, T, V) \]  \hspace{1cm} (B.19)

where \( \phi \) is the basin potential energy that maximizes the integrand, and can intuitively be understood to represent the mean potential energy expected upon instantaneous quenching from an equilibrium configuration randomly selected at temperature \( T \) \[13\]. Importantly, while the above conclusions have been derived under the context of equilibrium statistical mechanics, the same formulism can be applied to understand thermodynamic properties of the supercooled liquid phase. In this respect, the supercooled liquid is viewed as existing in a state of metastable equilibrium within the restricted domain of structurally amorphous inherent structures. In summary, the thermodynamic stability of given phase can be seen to be decomposed into three main components: namely, 1) the mean basin potential energy (or enthalpy), 2) the configurational entropy which is given by the logarithm of the number of distinct accessible basins, and 3) the mean intra-basin vibrational free energy, at the given temperature and operating conditions.
Appendix C. Additional Information on Model Generation, Validation, and Reproducibility

The validity of the liquid and glass model generation methodology summarized in Section 3.2 largely hinges upon whether thermodynamic and physical properties are reproducible from run to run, and whether time integration and temperature/pressure control parameters are appropriately configured. In order to test these various factors, a number of runs were conducted testing the sensitivity and stability of thermodynamic properties (system energies, enthalpies, volumes/densities, etc.) for Cu-Zr, Ni-Al, and Zr-Cu-Ni-Al systems under various numbers of atoms (ranging from 1000-10000 atoms), initial configurations (randomly permuted atoms in the pre-melted crystal state) and velocities (various seeds for random sampling of the Maxwell-Boltzmann velocity distribution), time-steps, melt times, and temperature/pressure damping parameters for NVT/NPT thermostats.

Results of this analysis indicated that the stability and reproducibility of melt properties is well insured beyond system sizes of ~5000 atoms. Structural, kinetic, and thermodynamic properties were found to possess little to no dependencies below time-steps of ~2 femtoseconds and melt times greater than ~2 million femtoseconds, with melt times conducted under these settings being well in excess of underlying (structural, enthalpic, etc.) relaxation times of liquid alloy melts in general. Under these conditions, choosing the standard condition for temperature damping constants to be ~100 times the time-step, and pressure damping constants of ~1000 times the time-step were found to be sufficient for insuring stable temperatures and pressures under minimal fluctuations.
Appendix D. Summary of GFA Influences and Correlators

The main influencing factors governing GFA can broadly be categorized as being related to either: 1) atomic mobility and transport, 2) chemical order and complexity, 3) topological order and complexity, and 3) thermodynamics and energetics. Disordered phase correlators relevant to each of these general factors are summarized in Table D.1 below.

**Table D.1: Disordered phase correlators relevant to GFA prediction**

<table>
<thead>
<tr>
<th>Atomic Mobility and Transport</th>
<th>Chemical Order and Complexity</th>
<th>Topological Order and Complexity</th>
<th>Thermodynamics and Energetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>kinetic and thermodynamic fragility</td>
<td>number of elemental components</td>
<td>free-volume / packing-efficiency</td>
<td>Configurational / mixing entropy</td>
</tr>
<tr>
<td>free-volume / packing-efficiency</td>
<td>Configurational / mixing entropy</td>
<td>icosahedral short-range ordering</td>
<td>binary and total enthalpies of mixing</td>
</tr>
<tr>
<td>atomic mobility mismatch and dynamic decoupling</td>
<td>atomic-size mismatch (&lt;12%)</td>
<td>tetrahedral close packing</td>
<td>free energy of mixing and partial de-mixing</td>
</tr>
<tr>
<td>dynamic heterogeneity</td>
<td>short-range chemical ordering (Warren-Cowley parameter)</td>
<td>medium-range chemical ordering and entanglement</td>
<td>glass-glass / liquid-liquid interface energy</td>
</tr>
<tr>
<td>dynamic-crossover temperature and stoke-Einstein</td>
<td>medium-ranged chemical ordering and entanglement</td>
<td>medium-range topological ordering and connectivity</td>
<td>metastability with respect to compositional fluctuations (Spinodal decomposition)</td>
</tr>
<tr>
<td>breakdown</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix E. Comparative Summary of Ni-Al and Cu-Zr GFA Predictive Indicator Results

Simulations of equimolar Ni-Al and Cu-Zr alloys conducted in Chapter 4 of this work allowed for the direct evaluation of several GFA predictive indicators. These results are summarized below in Table E.1 for comparative purposes; with values coloured ‘green’ if in accordance with expected trends based on underlying GFA differences, or ‘red’ if in contradiction with expected trends.

Table E.1: Summary of various GFA predictive indicators evaluated for equimolar Ni-Al and Cu-Zr alloys. Values are presented in ‘green’ or ‘red’ color if in accordance or contradiction with expected trends based on the significantly higher GFA of the Cu-Zr alloy.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ni-Al</th>
<th>Cu-Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ [K]</td>
<td>744</td>
<td>676</td>
</tr>
<tr>
<td>$T_m$ [K]</td>
<td>1557</td>
<td>1354</td>
</tr>
<tr>
<td>$T_{rg} = T_g/T_m$</td>
<td>0.485</td>
<td>0.505</td>
</tr>
<tr>
<td>$\Delta \mu_{lc} (T_g)$ [eV/atom]</td>
<td>-0.135</td>
<td>-0.116</td>
</tr>
<tr>
<td>$\frac{\Delta \rho_{lc}}{\rho_c} (T_g)$ [%]</td>
<td>7.60</td>
<td>2.75</td>
</tr>
<tr>
<td>$\frac{\Delta \rho_{lc}}{\rho_c} (T_m)$ [%]</td>
<td>10.0</td>
<td>4.08</td>
</tr>
<tr>
<td>$D^*$</td>
<td>2.07</td>
<td>1.58</td>
</tr>
<tr>
<td>$M$</td>
<td>61.4</td>
<td>75.5</td>
</tr>
<tr>
<td>$\alpha_p(T_g)$</td>
<td>-0.09</td>
<td>-0.14</td>
</tr>
<tr>
<td>Glass $&lt;0,0,12,0&gt;$ [%]</td>
<td>4.2</td>
<td>6.3</td>
</tr>
</tbody>
</table>