

Emerging Evidence of a Second Glass Phase in Strong to Ultra-Fragile Bulk Metallic Glass-Forming Liquids

Thesis by
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they.them.theirs

In Partial Fulfillment of the Requirements for the
Degree of
Doctor of Philosophy

The logo for the California Institute of Technology (Caltech), featuring the word "Caltech" in a bold, orange, sans-serif font.

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To the part of me I lost
And all the parts I found

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Your PhD is a fight. On the third floor of Keck there is a story that describes one's thesis defense as fighting a snake (Appendix E). It describes that the longer the time spent in your PhD, the smaller the snake you fight in your defense. But what they don't tell you is that some of us come in with a snake we are already fighting. Sometimes these are small battles, sometimes they are life or death. Mine were the latter. I entered Caltech with PTSD, anxiety, and depression. Through my time here I found myself, my chosen family, re-found my given family, and much more. Through communities of dance and climbing I found self expression, strength, and encouragement. Through my advisor's field of researchers he nurtured himself, I found camaraderie and family. Around the world in my research exchange in Finland I found how small this place really is and how connected we can be. Through all of it, I found a family, and that family saved my life.

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ABSTRACT

This thesis compiles three experimental works that provide evidence for distinct bulk metallic glass (BMG) phases across a range of kinetic fragilities. Motivated by An *et al.*'s computational discovery of a secondary heterogeneous glass phase in pure Ag and binary AgCu and CuZr, the thesis reports the distinct glass phases in the high and ultra-high fragile regime with a tunable $Pt_{80-x}Cu_xP_{20}$ system, and the kinetically strong $Ni_{71.4}Cr_{5.64}Nb_{3.46}P_{16.5}B_3$ (Ni208) BMG.

The high-fragility work utilizes direct measurement techniques for liquid configurational enthalpy as a function of temperature on anneal-equilibrated samples (Chapter 2). An apparent first-order glass-melting transition is revealed across kinetic fragilities ranging from $m = 60$ to over 90. **[These results are embargoed pending publication.]**

Investigation of a kinetically stronger Ni-based BMG connects the presence of the secondary glass to the embrittlement transition in Ni208 (Chapter 4). **[These results are embargoed pending publication.]**

These works provide compelling evidence for the existence of a secondary glass phase across the spectrum from strong to ultra-fragile glasses, and validates the initial computational discovery. This proves to be a significant work, as it presents direct experimental evidence of a novel phenomenon in metallic liquids, and presents a new solid-like glass phase.

PUBLISHED CONTENT AND CONTRIBUTIONS

- [1] Qi An et al. “The L–G phase transition in binary Cu–Zr metallic liquids”. In: *Physical Chemistry Chemical Physics* 24.1 (2022), pp. 497–506. ISSN: 1463-9076, 1463-9084. DOI: [10.1039/D1CP04157F](https://doi.org/10.1039/D1CP04157F). URL: <http://xlink.rsc.org/?DOI=D1CP04157F> (visited on 02/15/2022).
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- [6] Jong H. Na et al. “Observation of an apparent first-order glass transition in ultrafragile Pt–Cu–P bulk metallic glasses”. In: *Proceedings of the National*

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Chapter 1

THE HISTORY AND EVOLUTION OF BULK METALLIC GLASS

1.1 Metallic Glass and the Bulk Form

Traditionally, metals are ordered and crystalline, while disordered glasses are polymeric, molecular, or inorganic compounds such as oxides, chalcogenides, etc. Bulk metallic glasses (BMGs), however, are amorphous metal alloys, and were the first materials to bridge this gap. They extend metallic alloys to the amorphous state, and emerge with beneficial properties from each. The first metallic glass was achieved in 1960, when Duwez reported a Au-Si alloy that was splat quenched at $10^5 - 10^8$ K/s, yielding an amorphous foil $\sim 10\text{-}\mu\text{m}$ thick.[1, 2, 3, 4] This first amorphous metallic alloy would begin a new field of research; Metallic Glass (MG), and later, with slower cooled samples on the millimeter scale, Bulk Metallic Glass (BMG).

To achieve a successful BMG, relatively rapid quenching of the molten alloy is utilized to circumvent its natural tendency toward rapid crystallization. During quenching, the molten alloy must pass rapidly through a thermodynamic regime (Figure 1.1) where the liquid is metastable.[5] The sample must be undercooled below its equilibrium melting temperature or liquidus temperature, T_l , in the case of an alloy, while remaining in the liquid phase. This regime is termed the Super-Cooled Liquid (SCL). The SCL alloy is then cooled until atomic motion is arrested, and a configurationally frozen liquid or amorphous phase is achieved below the glass transition (T_g). Through the SCL, crystallization must be bypassed prior to

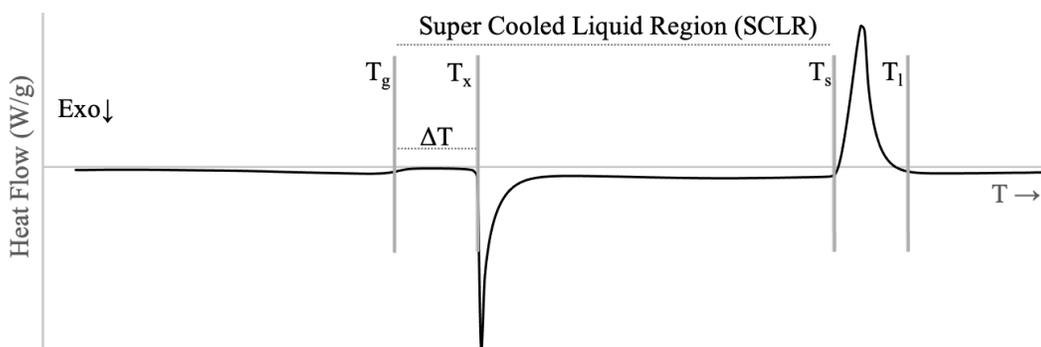


Figure 1.1: Representative thermal scan depicting characteristic transitions in BMGs.

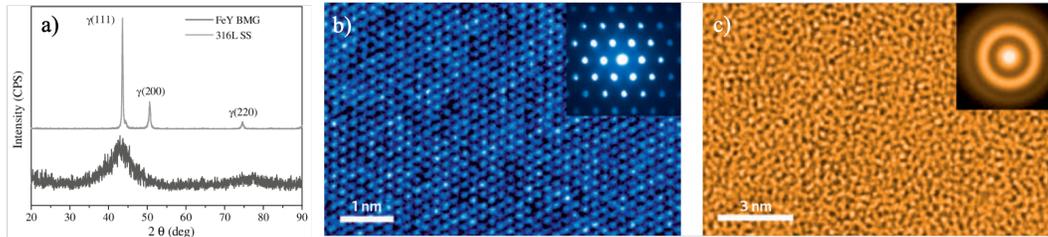


Figure 1.2: Visualization of ordered vs. disordered characteristics. a) Representative X-ray diffraction patterns for crystalline (top) and amorphous (bottom) material. TEM image and electron diffraction for an ordered material (b) and a metallic glass (c). Reproduced from Wang *et al.* (a) [6], and Jafary-Zadeh *et al.* (b,c) [7]. For b and c, copyright © 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>)

arriving at the glass transition.

Once cast to below T_g , the sample requires verification of its amorphous structure and lack of long-range order. This is most commonly displayed in X-Ray Diffractometer (XRD) scans and diffraction patterns by a broad diffraction band in place of crystalline peaks. High resolution Transmission Electron Microscopy (TEM) images are often used to visualize the presence or absence of atomic order. Figure 1.2a displays representative crystalline (top) and amorphous (bottom) XRD scans, while Figures 1.2b and 1.2c show typical TEM and electron diffraction for ordered and amorphous materials, respectively.[6, 7] From diffraction patterns, one can compute Radial Distribution Functions (RDFs) that report the distribution of atomic neighbor distances between pairs of atoms. The absence of periodicity (peaks) implies a lack of long range atomic order.

Metallic Glass Characteristics: Thermal and Mechanical Properties

Once quenched to ambient temperature, BMGs display characteristic thermal events on subsequent reheating from the glassy state (Figure 1.1).

In typical glasses, on passing through the Glass Transition Temperature, T_g , there is an endothermic increase in heat capacity accompanied by a change in the volume thermal expansion coefficient. T_g is traditionally defined as the temperature where the observed viscosity reaches 10^{12} Pa-s or 10^{13} Poise during cooling (or heating). Above T_g , atoms (or molecules) display increased mobility and the liquid exhibits the ability to "flow" under stress. It transitions from solid-like to fluid-like behavior.[8]

Above T_g , liquid fluidity increases rapidly (by orders of magnitude) over a narrow range of temperature. This temperature regime is utilized to reshape the material and produce net-shape parts as is done in glass blowing, blow molding, or injection molding.[5] The viscosity of 10^{12} Pa-s (often taken to define T_g) corresponds to the typical softening point of silicate glasses above which glass blowing can be implemented.[8]

Similar to other glass systems, BMGs can be formed and reshaped as temperature increases above the glass transition. However, given their metallic nature, there are marked differences. First, the glass transition of MGs occurs over a wide range of temperatures; T_g ranges from room temperature (e.g., for the Duwez Au-Si metallic glass) to as high as ~ 800 K for MGs based on refractory metals.[9, 10] This compares, for example, to a lower and smaller range of 60 - 500 K for traditional molecular and polymeric glasses.[11, 12] Second, while the glass transition is present across all glass systems, BMGs tend to crystallize more readily and undergo an accompanying distinct thermal event before melting; recalescence. Recalescence is an exothermic heat release from the relatively sudden atomic rearrangement from the liquid to crystalline phase transition. This occurs at a temperature designated as T_x .

Many traditional glasses exhibit very sluggish crystallization kinetics and display no distinct exothermic event or well-defined T_x . The region of liquid metastability during heating, $\Delta T = T_x - T_g$, thus tends to be smaller for BMGs than for many polymer, molecular, or silicate glasses, where crystallization often does not occur on any practical laboratory time scale between T_g and T_m . The relevant transitions and temperature regimes are illustrated by a representative BMG Differential Scanning Calorimeter (DSC) trace as shown in Figure 1.1.

Metallic Glasses exhibit certain unusual mechanical properties compared with traditional glasses and crystalline metals. For example, they have typical tensile strength several times greater than steel and other crystalline engineering metals. This is presumed to be due to the absence of dislocations and other extended defects that are responsible for plastic yielding and deformation in the case of crystalline metals. Metallic glasses deform by stress-induced activation of nano-meter scale local soft regions called shear transformation zones.[13, 14] Below T_g , deformation tends to become spatially localized and concentrated into bands called shear bands. The formation and operation of these shear bands under stress is the primary mechanism of plastic deformation in MGs. Unlike molecular and oxide glasses, MGs may ex-

hibit significant ductility under certain loading conditions such as compression and bending. In this case, one observes formation and operation of many shear bands throughout a macroscopic sample. In contrast, MGs exhibit little or no ductility in unconfined loading conditions such as pure tension. In a tensile test, metallic glasses tend to fail along a single narrow shear band inclined at an angle of 45 degrees with respect to the tensile axis. The fracture toughness (K_C) of metallic glasses is reported to vary over an extremely wide range from that of very brittle silicate glasses ($K_C \sim 1 \text{ MPa} - \text{m}^{1/2}$) to as high as that of tough steels ($K_C \sim 100 \text{ MPa} - \text{m}^{1/2}$).^[15] Above T_g , flow becomes delocalized and homogeneous much like flow in an ordinary liquid, albeit with a high viscosity. In this regime above T_g , metallic glasses can be shaped and formed in the same manner as thermoplastics.^[2, 16, 17, 18]

In summary, while MGs offer distinct improvements over traditional metals such as very high strength, they may also exhibit limited toughness and ductility, and ultimately experience catastrophic brittle failure; e.g., in tension. The tendency to crystallize easily in the supercooled liquid region means that relatively high cooling rates from the molten state are required to produce BMGs. The requirement for rapid cooling in turn limits the maximum dimensions of BMGs due to ability to extract heat on quenching. In practice, BMGs are limited to cast rods of diameter in the mm to cm range, or thin plates of similar thicknesses (Section 1.3). So similar to traditional metallurgy, much research in the field of BMGs is directed to addressing these limitations. Alloy development pursued the discovery of alloys that have greater resistance to crystallization, and that exhibit enhanced toughness and ductility, or other desirable attributes. Other areas of active study include oxidation resistance, magnetism, and ferromagnetism. Further, studies of BMG composites address brittle failure by utilizing crystalline dendrites in an amorphous matrix to arrest crack growth. This has resulted in increasing fracture toughness ten-fold.^[19]

This unusual combination of properties motivated research to investigate their fundamental origins. The remaining sections of this chapter outline the applications, underlying physics, formation criteria, and casting methods that took BMGs from microns thick to the bulk scale as Bulk Metallic Glass (BMG).

Applications

Following BMG discovery, many applications were explored. These applications span commercial and research sectors. Examples are included in Figure 1.3.

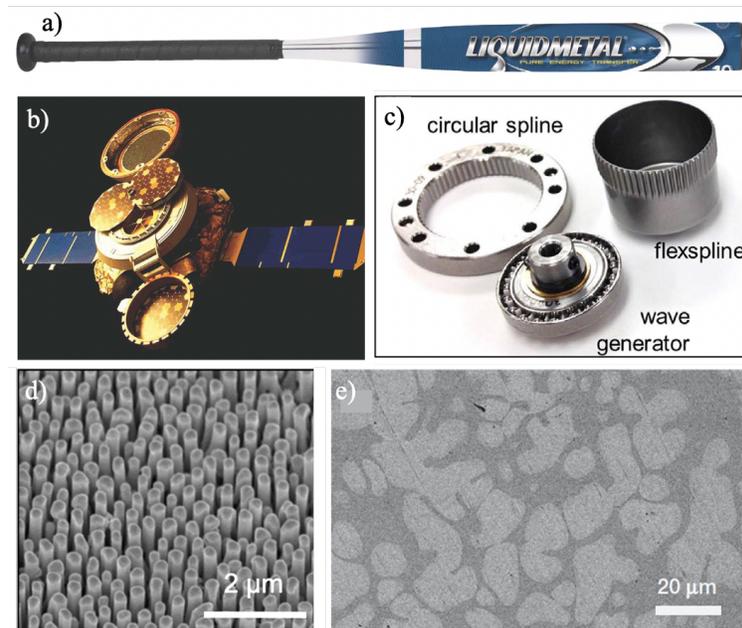


Figure 1.3: Visualization of select applications. a) A BMG-coated baseball bat by LiquidMetal Technologies [5], b) a BMG disc on the Genesis Mission as a solar wind collector [5], c) BMG flex splines for strain wave gears [20], d) thermoplastic formed BMG nano-rod for a subcutaneous blood glucose sensor [21], and e) a BMG matrix composite for increased toughness [22]. All images reproduced with permission. Image d: Reprinted with permission from [21]. Copyright 2017 American Chemical Society.

In the commercial sector, applications have been explored in sporting goods, consumer electronics, and medical applications.[5] Sporting equipment has included golf clubs, baseball bats, and tennis rackets with BMG coatings or frames. Consumer electronics applications have included injection molded and die-cast phone frames and casings for increased scratch, water, and dent resistance. In orthodontics, fabrication of dental brackets and appliances is being explored.

In the research sector, a Zr-based BMG was used as a collection device for the solar wind on the 2001 NASA Genesis Discovery mission.[23] The "flow" characteristics of BMGs have led to its use in additive manufacturing. NASA JPL has used cast net-shaped BMG strain wave gears for precision robotics on rovers for improved wear resistance.[20] Metallic glasses are an improved material for gearbox flexsplines due to BMG embrittlement resistance at the low temperatures encountered in space applications.[20]

When BMGs first emerged, it was hypothesized that a stronger, tougher, general-

use glassy “steel” was possible. But as time progressed and research developed, the most successful pursuits arose when BMG compositions and properties were tuned and selected *specifically* to meet particular goals and specifications in “niche” applications. For example, the most common and processable BMG alloys to date are the Zr-, Fe-, and Pt-based alloy families. Zr-BMGs (e.g., Vitreloy alloys) are the most widely studied BMG system and have the most widespread structural applications, while ferromagnetic Fe-base BMGs have been adopted in widespread use as soft magnetic materials in inductors and transformer cores, and Pt-based amorphous alloys have been used as a catalyst site for subcutaneous blood glucose sensors, to name a few niche applications.[24, 25, 21]

Since fine tuning of properties of BMGs is where they provide the greatest benefits, Section 1.3 describes how fundamental research developed standardized rules and procedures for achieving and identifying good metallic glass formers with desirable properties. These approaches, similar to applications, were informed by combining theories and methods of both crystalline metals and traditional amorphous materials. But to fully understand BMG casting, these theories and methods are first described in Section 1.2 below.

1.2 Classical Theory for Bulk Metallic Glass

Periodicity in *ordered* materials permits simplifying models and assumptions in theory development. These theories have underlain the advancement of our understanding of periodic crystalline materials in a broad range of fields; e.g., semiconductors, structural materials, Bloch’s theorem, etc.[26] Glasses in general and BMGs in particular — without long-range atomic order — do not lend themselves to such simplifications. A microscopic theory of the statistical mechanics of glasses has been developed based on the concept of potential energy landscapes (PELs). The PEL theory provides a microscopic basis for understanding the thermodynamic, kinetic, and physical properties of glasses. The basic results of PEL theory provide the basis for much of the work on metallic glasses in the present thesis. As such, it is important to provide an outline of the basic theory.

Potential Energy Landscape Description of Bulk Metallic Glass

Metallic glasses are described energetically by a Potential Energy Landscape (PEL). A PEL provides a topographic view of all the accessible potential energy states across a system of interacting particles (Figure 1.4). This potential energy is a function

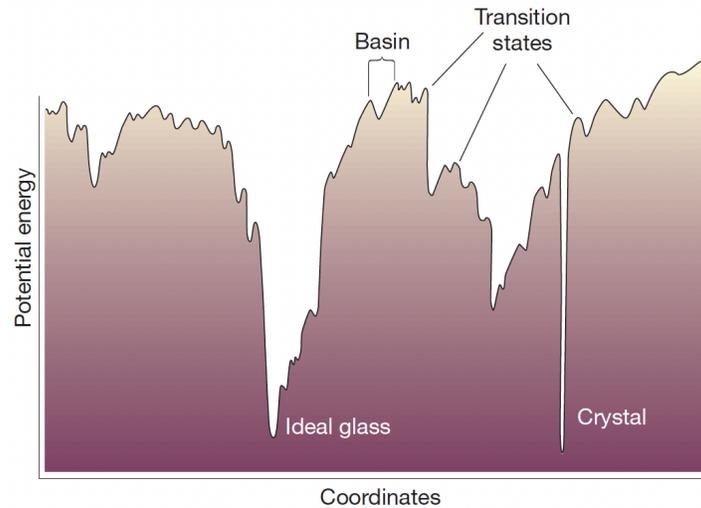


Figure 1.4: Representative PEL. Reproduced with permission from [28].

of the $3N$ atomic coordinates of all the atoms that comprise the system. These energies arise from pair interactions (or more generally, many-body interactions) between atoms, where the total potential energy is the sum of these interactions across all atomic pairs. Varied local environments and configurations yield different potential energies. A stable atomic arrangement corresponds to a local minimum in the overall potential energy whereby the force on each atom is zero. Such a local potential energy minimum is referred to as an inherent state (i.e., a state of energy in a $3N$ particle system) of the liquid/glass. Therefore, specific stable atomic configurations described by these minima are referred to as the inherent states of the PEL; where crystal atomic configurations have deeper wells and greater stability compared to typical amorphous inherent state structures.[27]

Movement around the PEL can be described as a sequence of transitions from one inherent state to another; excitations.[27, 29, 28] Elementary excitations over potential energy barriers move a system between its inherent state energy wells in the PEL. They allow for inter-basin hopping between the local minima, but are not energetic enough to move the system from a liquid inherent state to a crystalline state; relaxations discussed further in Section 1.2: Kinetic Behavior in the PEL, Relaxations. Glasses and liquids utilize this inter-basin hopping to achieve their characteristic configurational changes associated with flow. Upon heating above T_g , enough thermal energy is available to allow inter-basin hopping and internal movement between amorphous/liquid inherent states, but not enough to access a crystalline state or to access the higher energy states of a liquid above its melting

points (melting basin depth not shown in Figure 1.4).

In addition to PEL theory's effective description of the energetics of atomic configurations, it can be combined with statistical mechanics to determine thermodynamic state variables such as energy. It can be further refined by assuming separability of vibrational and configurational components for a more specific analysis, as discussed below.

Thermodynamic Application of PEL: Separable Configurational and Vibrational Components via the Canonical Ensemble

A key feature of PEL theory is that it allows for separation of configurational and vibrational components in thermodynamic functions. This occurs through a number of steps. First, with a PEL, a distribution of occupied inherent energy states is required to describe a system. A statistical distribution is chosen to describe the density of states (DOS); e.g., Gaussian, exponential, etc. Second, a partition function (Z) is required. Z is a function of temperature and microstate energies as a model of microscopic constituents of a system; i.e., number of particles, volume, particle mass. It relates these microscopic details to thermal quantities through its logarithmic derivatives. Third, the partition function type is selected. For this work, a canonical partition function is of practical use. The canonical partition function comes from the canonical ensemble that allows environmental heat exchange at fixed number of particles, volume, and temperature (the NVT ensemble). This applies to equilibrium conditions of BMGs at fixed T and is therefore useful here.

Combining these criteria, a distribution-defined DOS and the Canonical Z , the resultant separation is described through an example derivation of free energy, F .

Separability is achieved via the canonical approach to the partition function — where taking the log of the partition function for the Helmholtz free energy yields a sum of the exponential components (the log of factors is a sum); demonstrated below.

Separability arises from the derivative of

$$F = -kT \ln(Z), \quad (1.1)$$

where Z is the canonical partition function with a DOS coefficient;

$$Z = \int D(E) \exp\left[\frac{-E}{kT}\right] dE. \quad (1.2)$$

with E the energy of the system. When E is represented by a sum of its configurational and vibrational parts, the following results:

$$E = E_{Config} + E_{vib,har} + E_{vib,anh}, \quad (1.3)$$

where vibrational energies are further divided into harmonic and non-harmonic components.

When combining equations 1.1 - 1.3,

$$F = -kT \ln \left(\int D(E) \exp \left[\frac{-(E_{Config} + E_{vib,har} + E_{vib,anh})}{kT} \right] dE \right) \quad (1.4)$$

and using exponential and log manipulations

$$e^{x+y} = e^x \cdot e^y \quad (1.5)$$

$$\ln(e^{x+y}) = \ln(e^x \cdot e^y) \quad (1.6)$$

$$\ln(a \cdot b) = \ln(a) + \ln(b) \quad (1.7)$$

$$\ln(e^x \cdot e^y) = \ln(e^x) + \ln(e^y) = x + y \quad (1.8)$$

the thermodynamic functions emerge with distinguishable contributions from configurational and vibrational parts, and can be treated individually;

$$F = -kT \ln \left(\int D(E) \exp \left[\frac{-E_{Config}}{kT} \right] \exp \left[\frac{-E_{vib,har}}{kT} \right] \exp \left[\frac{-E_{vib,anh}}{kT} \right] dE \right). \quad (1.9)$$

While possible in this mathematical example, this separability is backed by theory and experimental evidence as well.

For the separable behavior, a key underlying assumption is that the average vibrational DOS does not depend on the energy of an inherent state minima. Thereby anharmonicity is avoided and the anharmonic approximation is not needed. This separation of vibrations from energy dependence allows for the decoupling of the vibrational and configurational parts from the canonical partition function, and full separation is possible come manipulation for the Helmholtz free energy.

For experimental evidence, Smith *et al.* reported direct *in-situ* measurements of the vibrational spectra of strong and fragile metallic glasses in the amorphous, liquid,

and crystalline phases in the vicinity of T_g . For both strong and fragile glasses, less than 5% of the total excess vibrational entropy was found in the glass and liquid phases over the crystal.[30] This provides experimental evidence that the excess entropy of metallic glasses is almost entirely configurational in origin, validating early theories that the glass transition is purely configurational.[31]

Through PEL assumptions, once separated, these components can be treated and analyzed independently.

Vibrational Component

The vibrational component is characterized by phonon frequencies and the phonon density of states. In the PEL, phonon frequencies arise from the curvature in the landscape along the various directions of the configuration space surrounding the local potential energy minimum. For $3N$ particles, there are $3N-6$ independent configurational coordinates (the 6 degrees of freedom associated with center of mass motion and system rotation are not vibrational degrees of freedom). This curvature matrix is the second derivatives of the PE with respect to the coordinates (x_i, y_i, z_i where “ i ” labels particles) and can be described as a dynamic matrix. Through analysis of this matrix via diagonalization and eigenvalue determination, one attains the normal modes and phonon DOS, respectively. In effect, the phonon frequencies go to zero when the curvature of the PEL goes to zero (an inflection point).[28] From the phonon DOS, the phonon free energy and vibrational entropy are defined as seen in Smith *et al.*[30]

With the vibrational component separated and a focus drawn to phonons, this can be used, for example, to deduce the sound velocity in a material. The sound velocity of long wavelength phonons is determined by elastic constants. Sound velocities can be measured using ultrasonic transducers where the long wavelength vibrational modes are sampled, and elastic constants calculated. Elastic constants are represented by phonons that collectively move large groups of atoms in phase space. While useful, the separated vibrational component will not be addressed in this work. In effect, the configurational component takes focus, and experiments to determine the configurational contribution to the free energy are explored in Chapter 2 of the thesis.

Configurational Component

In the PEL, the configurational part of the partition function is a sum of configurational energies over all minima. When separable from vibrations, and as seen in

work by Smith *et al.*, the glass transition at T_g is described as a purely configurational event. Thus, if heated from a relaxed glass state, the resulting enthalpy associated with the glass transition is purely configurational.

When isolated from the vibrational component, the configurational enthalpy is actually representative of the potential energy of the system. This is achieved since all of the experiments are done at ambient pressure. Strictly speaking, specific enthalpy $h = e + pv$, and changes in specific enthalpy (with respect to a reference state) can be expressed as $\Delta h = \Delta e + p\Delta v$.^[32] In our experiments at ambient p , the $p\Delta v$ term can be shown to be very small compared with Δe . As such, $\Delta h \sim \Delta e$ can be shown to be an excellent approximation (i.e., $p\Delta v$ is on the order of 10^{-3} compared to measured $d\Delta h$ values (Chapter 2). So $p\Delta v$ is neglectable to an accuracy of 0.1% or better. Assuming using all of v , where Δv is actually 10^{-2} of v .) In equilibrium at fixed T , kinetic energy is simply $1/2kT$ per degree of freedom. It follows that changes in configurational enthalpy (with respect to a reference state at fixed T) are equivalent to changes in the specific configurational potential energy of the system. This equivalence will be important throughout the discussion presented in Chapter 2 and is described in further detail in Appendix B.1.

A Gaussian Landscape and Thermodynamic Functions

The PEL is particularly useful for defining thermodynamic functions of amorphous materials. A widely used approach assumes a lack of energetic preference for atomic interactions or configurations. This results in a random spatial distribution of atomic configurations and random atomic interactions. Basically, the energy of inherent states is assumed to arise from a sum of random variables. This naturally gives rise to a Gaussian density of states (DOS) to represent the distribution of energies for the inherent state minima.^[27, 28] When applied to the canonical partition function, this yields an integral over a Gaussian distribution. The derivation from the Gaussian DOS in the canonical partition function to the Helmholtz free energy (F), entropy (S), internal energy (U), enthalpy (H), and heat capacity (C_p) are carried out and described in Appendix A, and are summarized below.

$$F = +kT \ln \sqrt{2}\sigma - \frac{\sigma^4}{kT} \quad (1.10)$$

$$S = -k \ln \left(\sqrt{2}\sigma \right) - \frac{\sigma^4}{kT^2} \quad (1.11)$$

$$U = \gamma - \frac{2\sigma^4}{kT} \quad (1.12)$$

$$H = U = \gamma - \frac{2\sigma^4}{kT} \quad (1.13)$$

$$C_P = \frac{dU}{dT} = \gamma + \frac{2\sigma^2}{kT^2} \quad (1.14)$$

When applying the Gaussian DOS for the configurational contribution, the resulting equations for the total crystal and liquid heat capacities (configurational + vibrational contributions) are:

$$C_{P,x}(T) = 3R + aT + bT^2 \quad (1.15)$$

$$C_{P,l}(T) = 3R + cT + dT^{-2} \quad (1.16)$$

where $3R$ is the Dulong-Petit heat capacity, and the components with a , b , and c coefficients are anharmonic contributions. Within the liquid heat capacity equation there is a liquid-specific configurational term, " dT^{-2} ," that arises from the Gaussian density of states assumption in the Gaussian Landscape Model; the last term of Equation 1.14.

Figure 1.5a fits experimental heat capacity with Equations 1.15 and 1.16. Assuming sufficient fit, enthalpy (Equation 1.13) and entropy (Equation 1.11) are plotted in Figure 1.5b and c, respectively. When inspecting the total entropy curve, an interesting phenomena appears; the Kauzmann Paradox. The Kauzmann Paradox arises in thermodynamic glass physics when comparing the total entropy of a liquid and crystal. At absolute zero, $T = 0$ K, the entropy of a solid phase should approach zero (Third Law of Thermodynamics). However, as seen in Figure 1.5c, when projected to 0 K, the SCL entropy extends below zero to negative values. Ostensibly, the liquid entropy would become negative and non-physical. But experimentally, the system arrests to a glass before this occurs. To this end, it is hypothesized the glass transition exists to circumvent this thermodynamic paradox. We discuss this apparent paradox in Chapter 2.

PEL theory provides a helpful picture to understand energetic states of glasses. But while providing a classical and fundamental approach to BMG thermodynamics, the Gaussian assumption leads to compounding problems as will be seen below.

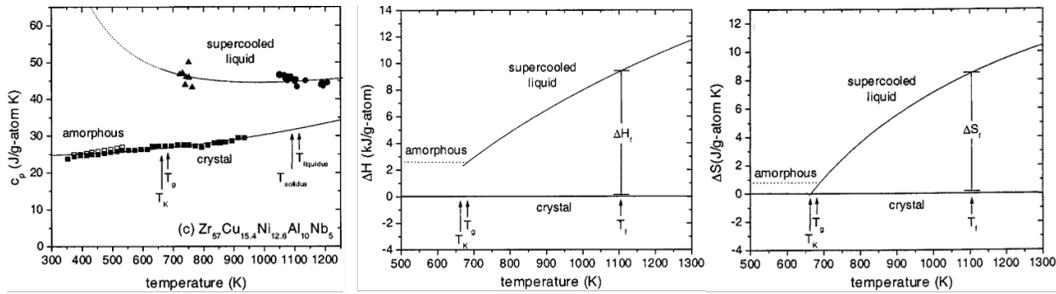


Figure 1.5: Thermodynamic Functions via the Gaussian Landscape. Heat capacity, enthalpy, and entropy are plotted in the first, second, and third components, respectively. Reprinted from [33] with the permission of AIP Publishing.

Issues Arise with the Gaussian Landscape

Upon greater inspection, the assumed Gaussian distribution of filled energy states is not representative of a glass system. This simplification describes the local potential energy distribution about each atom by assuming both a random spatial distribution and random interactions around the given atom. The resulting summation over multiple random atomic interactions leads to an assumption that the distribution is Gaussian at all energies. However, with these assumptions, multiple issues arise. In reality, a preferred and known absolute minimum is introduced at low temperatures; the crystalline state. Therefore, the potential energy of a configurational state must be bounded below, whereas a Gaussian distribution has no absolute lower bound. And while Equation 1.15 fits the glass and crystal heat capacity data (at temperatures where data are available) in Figure 1.5a, the SCL data varies widely from Equation 1.16 at low temperatures. The resultant T^{-2} dependence from a Gaussian DOS heat capacity induces a sharp upward curvature at low temperatures that does not well describe the SCL data.

Further compounding this issue of an approximate model, are inaccurate data. This data inaccuracy is three-fold. First, given BMGs have higher transition temperatures than traditional glasses, a Differential Thermal Analyzer (DTA) with a higher temperature range is necessary for measuring heat capacity, enthalpy, and related variables. Traditional glasses use a Differential Scanning Calorimeter (DSC), and this instrument reports high-quality heat capacity data which are then used to calculate further thermodynamic functions. This approach has been taken with BMGs using a DTA, but the different measurement method makes this more difficult and less accurate near T_g (Step Calorimetry). Choosing to measure heat capacity with a DTA leads to error, whereas directly reporting enthalpy is more accurate for this

apparatus. Thus, direct reporting enthalpy and calculating to heat capacity (by differentiation) is a necessary adjustment with a DTA.

Second, with the configurational dependence of glasses more recently established in 2017, the data in Figure 1.5 did not prioritize achieving a well-defined reference state. Without this reference state prior to measurement, each data point had a different energetic baseline value — leading to the wide vertical spread of SCL data in Figure 1.5a. Utilizing annealing for configurational and energy equilibration will lead to more consistent and precise measurements.

Third, for metallic glasses, there are limited data in the mid-range SCL due to the intervention by rapid crystallization. Additional data in this region could inform the proper curvature of the heat capacity equation. This region is particularly elusive to data measurement due to the center of the SCL having limited access from both above (under cooling below T_l), and from below (heating above T_g). Moving too far into this region for long times yields crystallization. Thus, a new method was required with heating rate, data sampling rate, and accuracy capable of acquiring data in this inaccessible region; to heat/cool and measure the material response before crystallization. In 2011, Rapid Capacitive Discharge Heating (RDH) was developed for this purpose. Since its inception, RDH has informed this data region for a number of alloys, and contributes to Chapter 2.[34, 35, 36]

These three shortcomings compound and create challenges when attempting to validate a Gaussian landscape model. There is the potential that the Gaussian DOS assumption leads to an apparent Kauzmann paradox as either an artifact of the failed Gaussian landscape model or from insufficient data to assess the model. As such, an improved experimental approach is required to properly assess the theory. The acquisition of better experimental data along with a test of the theory are explored in Chapter 2.

Kinetic Behavior in the PEL, Relaxations

Recalling the initial introduction of the PEL model, the energetics of atomic configurations were discussed, and the transitions between inherent states through excitations and relaxations were first introduced. This section will elaborate on these relaxations as how they enable sample equilibration.

In glass physics, atomic rearrangement has different features over key temperature regimes; the super cooled liquid and solidified glass. As determined by Johari and Goldstein, there are two distinguishable types of relaxations deemed α - and

β -relaxations.[37] α -relaxations (Maxwell relaxations) are primary relaxations associated with the irreversible rearrangement of atomic clusters. They describe atomic motion at higher temperatures, are non-Arrhenius, and describe vitrification and atomic motion arrest at T_g . α -relaxations are frozen-out below T_g , while β -relaxations remain operative. β -relaxations are secondary relaxations that describe more limited atomic motion that persists at lower temperatures. Such limited motion is often described as the rattling of the “cage” or “cage rattling” of neighboring atoms surrounding a given atom.[38] These β -relaxations tend to be more Arrhenius in character. With respect to the PEL, α - and β -relaxations both relate to movement between energy wells. Movements energetic enough to produce permutations of neighboring atom pairs are referred to as inter-basin hopping and are α -relaxations, while lower-energy intra-basin hopping between shallower local minima within a larger megabasin are β -relaxations. A series of β -relaxations may lead to less frequent α -relaxations.[39]

Both α - and β -relaxations are important to this discussion of structure and configuration because they enable structural rearrangements occurring at different temperatures. Annealing at or below T_g allows β -relaxations to occur without crystallizing. The active β -relaxations allow the glass to sample local regions of its state space to find a low-energy minima amongst the amorphous inherent structures. For anneals above T_g , α -relaxations take over and the material will ultimately crystallize given sufficient time dependent on the degree of atomic motion in the system. This time duration describes the metastability of the glass state. Metastability is relative to the relaxation time for configurational degrees of freedom. It can be quantified by the ratio of the time to crystallization to the Maxwell (configurational) α -relaxation time, $\tau_\alpha = \tau_M$. This ratio quantifies the ability of the glass sample to achieve configurational equilibrium prior to crystallization. It characterizes configurational equilibration of the glassy state, and therefore describes the applicability of thermodynamics. The Maxwell relaxation time near T_g is typically $\sim 10 - 100$ s and decreases rapidly with temperature above T_g .

The accessibility of both relaxations determines atomic mobility in the glassy/liquid states.[27] This in turn is related to Angell’s Kinetic Fragility of the liquid, and is discussed below.

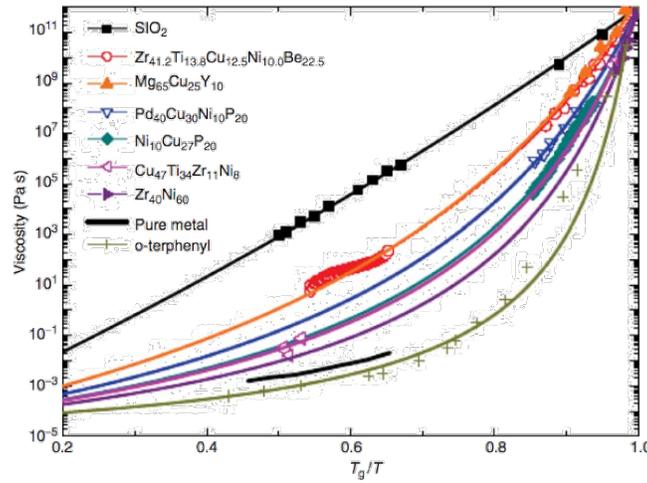


Figure 1.6: Angell Plot: Log Viscosity vs. normalized temperature. The slope as T_g is approached upon cooling indicates the Angell fragility parameter, m . Reprinted with permission from [40].

Kinetic (Angell) Fragility and Glass Quality

Kinetic (Angell) Fragility describes the rate of increase of atomic mobility as temperature increases above the glass transition temperature. It is closely correlated with the *deviation* of viscosity *from* simple thermally activated Arrhenius behavior. Arrhenius behavior (of atomic mobility or atomic diffusion) is characterized by a single activation energy:

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (1.17)$$

and viscosity, η :

$$\eta = A \exp\left(\frac{E_a}{k_B T}\right) \quad (1.18)$$

where k , R , A , E_a , k_B , and T are respectively the rate constant, universal gas constant, pre-exponential factor, activation energy, Boltzmann constant, and absolute temperature in Kelvin.[1, 41] In Figure 1.6, Arrhenius behavior corresponds to a straight line, whereas actual liquid viscosities exhibit an increasing curvature and deviation from an Arrhenius law. The Angell fragility parameter, m , quantifies this deviation and is defined as the slope of each curve as the glass transition is approached from above (Figure 1.6). Angell defined m as:

$$m = \left(\frac{\delta \log_{10} \eta}{\delta(T_g/T)} \right)_{T-T_g} \quad (1.19)$$

and describes the extent of atomic diffusion near the glass transition via the derivative of the logarithm of viscosity with respect to (T_g/T) . [2, 1]

Liquid fragility m plays a critical role in successful vitrification of a liquid. [8] “Strong” liquids with typical $m < 50$ have limited atomic mobility in the SCL region, and therefore often readily freeze into an amorphous phase. Their sluggish kinetics tend to yield lower critical cooling rates for glass formation that are advantageous for casting bulk samples, millimeters or centimeters in dimension. Most early BMG research focused on strong glass-forming liquids, and data for such systems dominate the metallic glass literature. However, “fragile” glass-forming liquids with typical $m > 60$ tend to crystallize more rapidly in the SCL region and therefore tend to be poor glass formers. They generally require higher critical cooling rates than can be achieved by common quenching methods, and therefore sample dimensions tend to be limited. Fragile glasses tend to crystallize more readily on reheating above T_g and thus require additional care in casting and testing. As such, published physical property data on fragile liquid glass formers are limited and such liquids have thus far been poorly characterized. [19]

Classical Theory Summary

The combination of metal and glass physics creates a multifaceted and interdisciplinary foundation. The PEL informs thermodynamic models, albeit with some drawbacks. There remain possible improvements in thermodynamic models and data collection, potentially in the elusive high-fragility regime. Even so, these foundations inform casting requirements and parameters such as composition and chemistry, thermodynamic and kinetic quenching conditions, methods, and more as described in the next section.

1.3 Formation Criteria

Casting a successful BMG requires fine chemical, thermodynamic, and kinetic control. This combines the traditional metallurgy and traditional glass physics established above. These controls summarized succinctly, BMGs are metal alloys that are quenched from the melt such that crystallization is avoided and the product is retained in the meta-stable amorphous state.

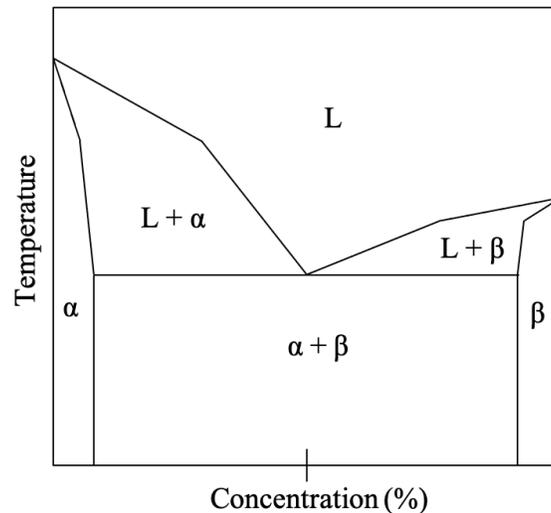


Figure 1.7: Representative Eutectic Diagram.

Chemistry Controls

In 2000, three factors were identified that inhibit crystallization for BMG formation; 1) multicomponent alloys of at least three elements, 2) atomic size mismatch of over 12% in the constituent atoms, and 3) negative heats of mixing between the three primary elements.[42, 43, 44] These factors stem from the “confusion” principle, preventing ease of atomic ordering, and energetic favoring of the liquid over the crystalline state, respectively. To promote application-specific properties in the cast glass, these factors prove useful. For example, one might emphasize an element, say Fe, for its magnetic properties. From there, adding two or more metallic elements or nonmetals with features that promote glass formation (e.g., useful atomic size mismatch or negative heats of mixing with Fe) provides a practical basis. However, while these rules are a useful starting point, many additional considerations are necessary for developing promising alloys for BMG formation.

Thermodynamic Factors — Eutectics

From a thermodynamic point of view, vitrification requires a quench of the overheated alloy melt. The melt must be cooled through the supercooled region below the liquidus/solidus temperature, and down to the glass transition temperature before crystallization can occur, effectively freezing the atomic liquid in place as a glassy solid. Essentially, the undercooled liquid must be frozen while avoiding the nucleation and growth of crystalline phases.

In a typical phase diagram, this quench follows a vertical downward path from the equilibrium liquid to the low-temperature amorphous solid.[45] Below the liquidus curve, (T_l), the driving force for crystallization increases monotonically with undercooling $T_l - T$. Crystallization results in a drop in free energy which increases with the degree of undercooling $T_l - T$ until one reaches an undercooling $T_l - T_g$ at the glass transition. In a eutectic phase diagram, the eutectic composition has a characteristically depressed liquidus temperature compared to the melting points of the atomic constituents (Figure 1.7). Turnbull first pointed out the importance of the ratio T_g/T_l in achieving glass formation. In the literature, this ratio is referred to as the reduced glass transition temperature or Turnbull's parameter, t_{rg} . He noted that at a eutectic composition, this ratio tends to display a maximum (versus composition). Further, he pointed out that when this ratio reaches a critical value of $\sim 2/3$, easy glass formation is to be expected. This is now referred to as Turnbull's criterion.[8]

It is now well established that vitrification of metallic alloys is most easily achieved in multicomponent alloys with compositions located near deep eutectic features in the alloy phase diagrams. When choosing between eutectic systems, deeper eutectics where T_g/T_l exceeds ~ 0.6 have been found to allow for more stable undercooling of the liquid and easy formation of BMGs. Although not a strict rule, the Turnbull criterion is generally a useful and simple predictor of glass forming ability in metallic systems. The alloys discussed in this thesis are excellent examples of deep eutectic alloys where $t_r \sim 0.6$ or greater.

Kinetic Controls

When quenching an alloy from temperatures above melting, a crystal forms if the material is not cooled at a sufficient rate to beat crystallization. The kinetic aspects of glass formation are described by a Temperature-Time-Transformation (TTT) diagram. TTT diagrams show the kinetics of crystallization in a 2-dimensional space of temperature and log time (Figure 1.8). With respect to temperature, the resultant phases are broken into four zones — Liquid, Supercooled Liquid (SCL), and Glass, with Crystals grown in the SCL given sufficient time. The curved border between the SCL and crystal is referred to as the "crystallization nose" or "nose." [34]

At time zero, at the top left of Figure 1.8, two overall behaviors emerge, i) the melt is quenched fast enough such that crystallization is fully avoided and the sample is successfully vitrified (Figure 1.8; $-\dot{T}_{glass}$), or ii) any quench rate eclipsed by the

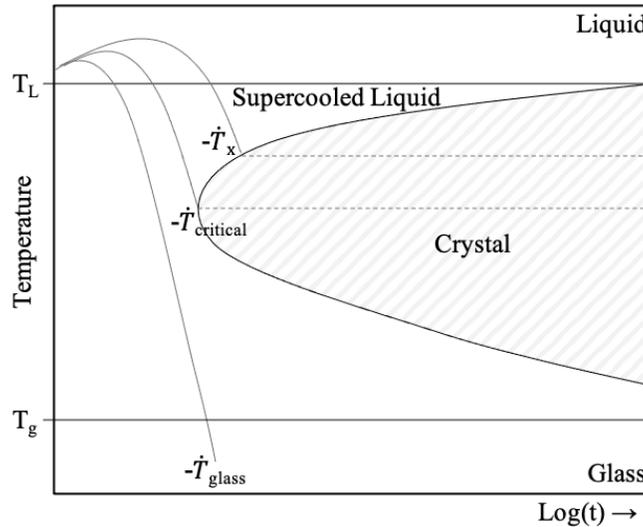


Figure 1.8: Representative Temperature-Time-Transformation (TTT) diagram where $-\dot{T}_{glass}$, $-\dot{T}_c$, and $-\dot{T}_x$ are cooling rates achieving a glass, the critical cooling rate, and a representative cooling rate where sample crystallizes, respectively.

crystallization nose is interrupted by nucleation given too long of a cooling time, and crystallization occurs within the sample (Figure 1.8; $-\dot{T}_x$). The cooling rate separating these two behaviors is defined as the critical cooling rate $-\dot{T}_{crit}$. In order to successfully vitrify the quenched melt, the crystallization kinetics of the sample need to be sufficiently sluggish or the casting method be sufficiently fast (i.e., quench rate faster than $-\dot{T}_{crit}$). Additionally, dependent on the regime of fragility, strong vs. fragile, the casting method and or sample dimensions must be selected accordingly.

Pre-Quench Controls

Additional factors that influence successful glass formation are overheating and fluxing. Overheated samples, samples taken at least 100°C over the liquidus temperature before quench, are found to exhibit better glass forming ability than those taken only slightly over their melting point.[5] This is presumably a result of melting any foreign particles such as oxides, etc.[8] Also, fluxing with boron oxide for long times increases glass-forming ability.[25] Both details are currently correlated with reduction of oxide-induced crystal nucleation sites. The former is believed to melt the oxides before quenching, and the latter to remove the oxides during alloying.[46]

While the underlying physics behind the benefit of overheating is not fully understood, Chapter 4 on a Ni-glass will address the effect of overheating on BMG embrittlement and its origin.

Method	Cooling Rate (K/s)	Sample Geometry	Sample Dimension
Splat Quenching	$10^5 - 10^6$	Circular foil	2-cm x 10- μ m
Quartz Tube/Water	14	Rod or capillary	mm to needle
Injection Molding	10^2	Die cut	mm
Counter Gravity	$10^1 - 10^2$	Die cut	cm
Arc Melt/Suction	$10^1 - 10^2$	Rounded	cm
Air Quench	1 - 10	Any	Any

Table 1.1: Summary of method cooling rates and respective practical geometries and dimensions.[47, 48, 49, 50]

Methods Addressing Kinetic Quench Requirements

When selecting a quenching method, multiple parameters must be discussed; the cooling rate must be sufficiently fast ($> -\dot{T}_c$), and the required sample geometry and dimensions must be specified.

Cooling rates range from $10^5 - 10^6$ K/s for splat quenching, down to 1 – 10 for air quenching. Table 1.1 column 2 summarizes common casting methods and their achievable cooling rates. For geometry, while fastest, splat quenching only yields 2-cm x ~ 10 - μ m thick foils; only practical for select uses. Common practical geometries include rods and capillaries through water-quenching in quartz tubes, and injection casting achieves cylinders, plates, bars, wedges, etc. via die-cut copper molds. Table 1.1 column 3 summarizes the geometries capable per casting method.

To achieve greater sample dimensions, stronger glasses with high Turnbull parameter (t_{rg}) and associated slower critical cooling rates make more methods accessible. However, when sample kinetics are sufficiently fragile, atomic diffusion must be suppressed at deep undercooling. The required faster critical cooling rate can be accommodated by employing smaller sample dimensions. Essentially, the rate of heat removable typically scales with the inverse square of sample thickness/diameter according to the solutions of the transient Fourier heat flow equation. Quartz-drawn capillaries are frequently used to achieve the smallest possible sample rod diameter for quenching ultra-fragile glasses. Table 1.1 column 4 summarizes the dimensions possible per casting method.

All these details work in concert to predict and achieve successful vitrification of a quenched melt. It is also noteworthy that more intricate net shaped samples are possible by use of post-casting methods that exploit the glass transition and BMG formability. These include thermoplastic forming (TPF) and additive manufacturing (3D printing) to build up more complex shapes.[51, 52] Thermoplastic forming takes

a pre-cast BMG rod, heated above T_g , and a force applied to induce flow into a mold. This method was used, for instance, to cast nanopatterned BMGs for a subcutaneous blood glucose biosensor.[21] A single BMG rod formed both the substrate and nonopillars ~ 200 -nm in diameter.[21] 3D printing of BMG material deposits the molten alloy in sequential layers to form a 3D structure, where the cooling rate of individual layers is determined by the layer thickness. In both cases, the sample cools before crystallization intervenes and remains amorphous.

Description for Glass Quality — Glass Forming Ability

The natural interplay between heat removal rate and sample dimension gives rise to the synonymous metrics of critical casting thickness, critical rod diameter, and glass-forming ability (GFA). GFA is reported in terms of the maximum achievable fully amorphous rod diameter (or plate thickness). This is determined in practice by identifying amorphous characteristics (by XRD, DSC, electron microscopy, etc.) at increasing rod diameters until a detectable level of crystallinity is present (i.e., XRD peaks appear or a calorimetric T_g or T_x disappear).

Formation Summary — Taking Metallic Glass to the Bulk Form

Due to the collaborative nature of these factors, some alloy systems and compositions form glasses more readily than others. Tuning the aforementioned formation controls led early research to increase glass quality, qualified by max achievable sample thickness. These methods resulted in the growth from the first AuSi 10- μm foil to Bulk Metallic Glass, millimeters in dimension.

1.4 Transition Types and Melting Criteria

While initial descriptions of BMG transitions (T_g, T_x, T_m, T_l, T_s) in Section 1.1 are useful, further discussion is necessary to better support Chapters 2 and 3.

Transition Types — Thermodynamic Classifications

In 1933, Paul Ehrenfest proposed a classification system for phase transitions. Based on the thermodynamic free energy and other state variables, transitions are labeled by the lowest derivative for which the free energy exhibits a discontinuity at the transition (phase boundary); where the Gibb's free energy is a function of independent thermodynamic variables (T, P, H, c , etc.).[53] A transition that shows a discontinuity in the first derivative of the free energy is labeled a first-order phase transition, and similarly for a discontinuity in the second derivative; a second- or

der phase transition.[54] In Ehrenfest's classifications, there could theoretically be third, fourth, and higher-order phase transitions, but only first- and second-order transitions are discussed here.

These discontinuities in free energy derivatives have physical meaning. Typical first-order transitions between solid, liquid, and gas have a discontinuity in the first derivative of free energy with respect to pressure. This translates to a discontinuous change in molar volume or density at the transition.[54] An example of a second-order transition is the ferromagnetic phase transition in iron and other metals where the derivatives are taken with respect to applied magnetic field strength, H . This transition shows a continuous change in magnetization across the phase boundary (first derivative), but reveals a discontinuity in magnetic susceptibility (second derivative).[45]

While useful, not all transitions fit into Ehrenfest's classification. For example, the superfluid transition in liquid He and other transitions are characterized by power law or logarithmic singularities in the second derivatives of the free energy (e.g., heat capacity, susceptibility, etc.) at the critical temperature, as opposed to simple discontinuities.[45] These are often referred to as λ -transitions. Such transitions are unclassifiable by Ehrenfest's classification scheme. Thus, these classifications were replaced by a similar but simplified naming convention that does account for these transitions.

Modern classifications use the same names as Ehrenfest's historical convention, but with updated definitions. First-order transitions are now described as having a latent heat — energy per volume is either absorbed or released at a fixed temperature. Transitions between solid, liquid, and gas phases remain first-order in this classification. Second-order transitions are also called continuous or order-disorder transitions, and exhibit a decay in a correlation length across the critical point.[45] Examples include ferromagnetic, superconducting, and superfluid transitions.

But when compared mathematically, both naming schemes describe various phenomena in similar ways:

For first-order transitions, when $G(T, P)$ is continuous and $S = -(\delta G/\delta T)_P$ or $V = -(\delta G/\delta P)_T$ are discontinuous, there is a latent heat and/or density change, respectively. For a second-order transition, when $G(T, P)$ is continuous as well as $S(T, P)$ and $V(T, P)$, discontinuities in the second derivatives of $G(T, P, N)$ describe discontinuities in the response functions for heat capacity, isothermal compressibil-

ity κ , and the thermal expansion coefficient, α :[\[45\]](#)

$$\begin{aligned} C_P &= T \left(\frac{\delta S}{\delta T} \right)_P &&= -T \left(\frac{\delta^2 G}{\delta^2 T} \right)_P \\ \kappa_T &= -\frac{1}{V} \left(\frac{\delta V}{\delta P} \right)_T &&= -\frac{1}{V} \left(\frac{\delta^2 G}{\delta^2 T} \right)_T \\ \alpha &= \frac{1}{V} \left(\frac{\delta V}{\delta T} \right) &&= -\frac{1}{V} \left(\frac{\delta^2 G}{\delta T \delta P} \right) \end{aligned}$$

The liquid/glass transition as observed experimentally displays a continuous change in viscosity at T_g , an apparent jump in the volume thermal expansion coefficient and heat capacity.[\[55\]](#) These sudden observed changes at T_g are what make detection of the glass transition possible in a DSC or Thermomechanical analyzer (TMA). However, these changes are also observed to depend on heat/cooling rates. There has been an ongoing debate in the literature over whether the glass transition is a purely kinetic transition or whether there exists an underlying thermodynamic phase transition. Further, it is also known that the presence of disorder can broaden a first- or second-order phase transition. As a result, there has been further debate as to whether the glass transition might be viewed as a broadened first-order transition or how it might be described. The question of whether the glass transition is characterized by an underlying thermodynamic transition is explored in [Chapter 2](#). Further context on identifying this transition as a type of melting transition is discussed there.

Additional Melting Criteria

In addition to the thermodynamic description of melting (a latent heat), two more criteria have been developed and described in the literature. The Lindemann and Born melting criteria focus on different aspects of melting — Lindemann on vibrational instability and Born on elastic rigidity loss. The Lindemann melting criterion indicates that melting occurs via a vibrational instability — such that a material will melt when the average amplitude of thermal vibrations exceeds some critical fraction of the interatomic distances.[\[56\]](#) Essentially the vibrations will cause motion greater than intermolecular interactions will support. The Born melting criterion focuses on the loss of elastic rigidity upon melting as quantified by the loss of a

finite shear modulus. Upon heating, a solid can no longer support shear stress; it has lost rigidity. In this approach, melting is viewed as a "rigidity catastrophe." [57]

Liquid/Liquid Transitions in Experiment and Computer Simulation

While common phase transitions occur between the three states of matter — solid, liquid, and gas — there also exist transitions within these states of matter, i.e., Intra-phase transitions. Such transitions may involve both ordered and disordered materials and occur when a solid-solid or liquid-liquid transition phase boundary is crossed within a phase diagram. An ordered solid can have various crystal or amorphous structures (polymorphism), an amorphous material can have multiple disordered structures (polyamorphism), and a liquid may exist in two distinct phases (liquid polyamorphism). Such transitions are identified by changes in thermodynamic or structural characteristics as one crosses the phase boundary. Primary polymorphism identifying tools include DSC and X-ray diffractometry, while Raman spectroscopy, thermomicroscopy, and other methods are used depending on the material. [58]

These transitions occur in solids and liquids. Notable examples are as follows. For solid-solid transitions, ice has 19 polymorphs, with three different amorphous structures. [59] The structures, identified via calorimetry and neutron powder diffraction, were formed using varying pressure and other techniques, and the phases have distinct structures and densities. [59] Liquid-liquid transitions are also observed, but lack distinct structural differences as found in solids. These transitions occur between states of disorder within the liquid phase and are often observed using thermal DSC scans. Recent research has established a liquid-liquid polymorphism as a key component in the pharmaceutical industry. Mannitol, a diuretic to reduce pressure inside the eye or around the brain, is the first pharmaceutical that utilizes a lower-energy polyamorph for increased aqueous solubility for drug delivery. [60]

While the phrase "liquid-liquid" transition is generally limited to the liquid phase, polyamorphs may exist for any non-crystalline material; i.e., glasses, other amorphous solids, super-cooled liquids, as well as typical conventional liquids or fluids. So within the liquid-like amorphous-structured solid phase, glass-glass transitions are possible. While glass-glass transitions are often difficult to identify, discontinuous property changes are a strong indicator of a phase transition. For example, work by Ketkaew and Schroers *et al.* observed an abrupt mechanical glass-glass toughening transition. They saw notch fracture toughness displaying an abrupt change as

a function of a well-controlled fictive temperature (describing average glass structure).[61] Through this, they identified how to achieve the two glass states with different properties. The distinct ductility and hardness across the phase boundary were tied to control of the fictive temperature by annealing. This transition potentially underlies the relatively abrupt embrittlement observed during processing of BMGs.[61] Once discontinuous properties are identified, annealing, deformation, or other processing may be used to reproducibly create the two different phases. This method of discontinuous properties correlated with phase transition will be used in Chapter 4 to explore the underlying cause of the embrittlement transition in Ni-based BMGs.

While discontinuous properties provide evidence of an intra-glass transition, the thermodynamics are particularly difficult to identify due to the metastability of the supercooled region. While experiments allow up to 20% undercooling of a BMG, the metastable samples crystallize rapidly the deeper the undercooling.[62] Thus, direct observation of evidence for a thermodynamic transition requires high-speed techniques such as Flash DSC (FDSC) or, alternatively, computational methods wherein much shorter time scales can be probed.

Experimental work has used FDSC to probe glass-glass transitions in the SCL. Schawe and Loeffler *et al.* identified two monolithic polyamorphs in Au-based quinary and quaternary BMGs.[63, 64] They used FDSC to access the heating rates necessary to melt the intermediate metastable phases within the SCL. They termed the two glass states a self-doped glass (SDG) and a chemical homogeneous glass (CHG), each with their own crystallization nose in a TTT diagram.[63] Shen *et al.* describes a secondary Metallic Glacial Glass (MGG) arising from a first-order transition in the SCL.[65] They probed a quaternary La-glass and report the MGG forming below the crystallization nose through FDSC.[65] It is important to note that generally, as the number of elements in a BMG decreases, the fragility increases. The FDSC works explored five- and four-element BMGs and found secondary glasses by utilizing high heating rates. However, it is hypothesized that within the elusive high-fragility regime, there may exist polyamorphs as secondary glass phases. To achieve successful analysis of high and ultra-high fragility samples, the sample kinetics require even faster methods than FDSC. In a collaboration with the author, An *et al.* used molecular dynamics to probe this metastable deep-undercooling regime for secondary glass phases in binary and single-element BMGs.

An *et al.* investigated pure Ag, and binary AgCu, and CuZr using Molecular

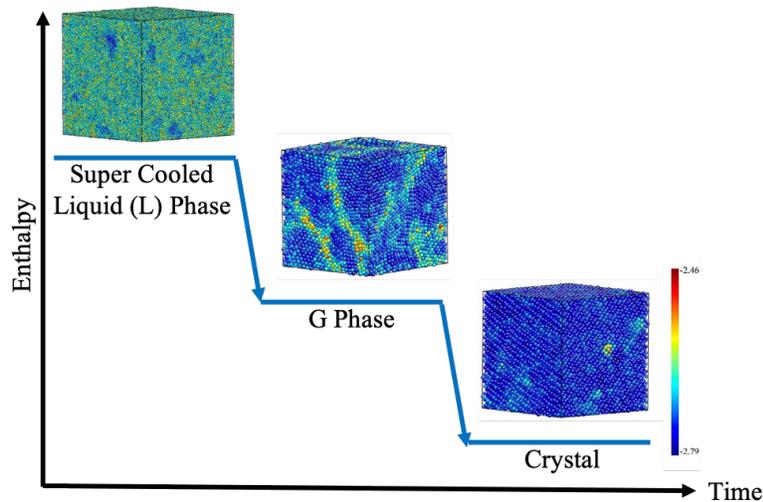


Figure 1.9: Energetic coordinate diagram for the traditional BMG phase (L glass), the secondary glass (G) phase, and the crystal of pure Ag. Figure recreated from [62].

Dynamics Simulations. They were the first to report and identify the heterogeneous G-phase, and define its first-order liquid-liquid transition to the traditional liquid-like L-phase metallic glass. This secondary glass phase, termed the G-phase, is a heterogeneous energetic metastable intermediate phase that lies thermodynamically between the traditional homogeneous SCL (L) glass and the equilibrium crystalline phase (Figure 1.9). It forms via a first-order freezing transition from the L-phase liquid with a latent heat and discontinuous entropy change. The transition was shown to be reversible, with the G-phase “melting” along a coexistence curve to the L-phase liquid. The heterogeneous G-phase structure is composed of ordered core regions surrounded by disordered liquid-like regions with consistently higher configurational enthalpy (Figure 1.9). The core regions exhibit local short-range order on a scale of ~ 1 -nm resembling nanocrystals, but with distinct curvature in the atomic planes along with stacking faults and point defects. The apparent size of the ordered cores varied with temperature and composition (in the case of alloys). The L-G transition is suppressed by the binary alloy systems with a reduced-ordered core size and heterogeneity length scale, along with a smaller latent heat for the L-G transition. The heterogeneity length scales were 4, 2, 1.8, and 1.5-nm for pure Ag, AgCu, Cu_7Zr_3 , and Cu_2Zr , respectively. Core regions exhibit fcc/hcp and icosahedral short-range order for Ag and AgCu (fcc/hcp) versus CuZr (icosahedral) cases, respectively. The G-phase is predominantly disordered, where ordered cores

contribute only 25% to overall local structure. The more-ordered solid-like G-glass exhibits persistent long-range elastic rigidity with a finite shear modulus as compared with the more fluid-like L-phase. Compositionally, the G-phase shows the structural heterogeneity as independent of chemistry or chemical separation in pure Ag.[62] In the binary alloys, AgCu revealed similar average composition across the heterogeneous G-phase structure, but wider variance from the L-phase.[66] The CuZr alloys identified that chemistry is not correlated with the L-G transition, though there is some spatial heterogeneity over the whole sample.[67]

These secondary glass works provide an important broader context for the findings throughout this thesis. The details of the L-G transition as revealed in the simulation work are related to the experimental results of Chapters 2 - 4, and will be expanded on further there. The results of this thesis are compared back to the G-phase and MGG to represent the simulation and experimental works, respectively. These are described together, as it is hypothesized that the SDG of Schawe and Loeffler's work and the metallic glacial glass (MGG phase) of Shen's work are essentially equivalent to the An *et al.*'s G-phase. Throughout the thesis, the primary and secondary glasses will be referenced by the terms L-, traditional-, and liquid-like glass/phase, and G-, ordered-, or solid-like glass/phase, respectively.

1.5 Motivation

This introduction has provided a summary of the important theoretical concepts and experimental background related to the nature of the glass transition in general and metallic glasses in particular. In addition, each section outlined particular shortcomings, inaccuracies, or a lack of sufficient understanding. These now become the motivations for this thesis:

1. Insufficient data both at high fragility and in the SCL yield a limited understanding of metallic glasses;
2. Current thermodynamic methods collect data from a non-equilibrium state, yielding erroneous data;
3. Inaccuracies of the Gaussian Landscape model in PEL theory require a new DOS representation to accurately describe data;
4. Incomplete understanding of BMG embrittlement;

5. Uncertainty of how the secondary G-phase glass manifests across experimental glass fragility.

Chapter 2 addresses motivations 1 - 3 with analysis of ultra-high fragility $Pt_{80-x}Cu_xP_{20}$ in a well-established ground state. The work presents a systematic experimental investigation of the configurational thermodynamics of the undercooled liquid as one approaches the glass transition. By accurate direct measurements of the liquid configurational enthalpy as a function of temperature, we are able to accurately determine the thermodynamic state functions of the undercooled liquid as the glass transition is approached. We find that the traditional Gaussian PEL model fails to describe the configurational thermodynamics of these ultra-fragile liquids. With increasing fragility, the glass transition becomes progressively sharper and remarkably evolves into an apparent discontinuous first-order phase transition with a latent heat and discontinuous change in configurational entropy. In this high-fragility limit, the glassy phase appears to display first-order “melting” in much the same manner as crystals melt.

Chapter 3 addresses motivation 5 by investigating the mechanics, structure, and thermodynamics on either side of the anneal-induced transition proposed in $Pt_{80-x}Cu_xP_{20}$ (Chapter 2). **[These results are embargoed pending publication.]**

Chapter 4 addresses motivations 4 and 5 with a kinetically stronger glass system, $Ni_{71.4}Cr_{5.64}Nb_{3.46}P_{16.5}B_3$ (Ni208) with $m \sim 54$, and its observed embrittlement transition. **[These results are embargoed pending publication.]** In effect, this chapter explores how the second glass phase in high-fragility PtCuP may extend to a stronger glass system.

Chapter 2

THE EMERGENT FIRST-ORDER PHASE TRANSITION IN ULTRA-FRAGILE $Pt_{80-X}Cu_XP_{20}$ BULK METALLIC GLASS

2.1 Abstract

The following chapter reports the experimental configurational thermodynamics of a highly-fragile near-eutectic $Pt_{80-X}Cu_XP_{20}$ BMG system. When X is decreased from 27 to 14, samples maintain bulk glass-forming ability, display increasing fragility to the ultra-fragile regime ($X < 17$), and show an increasingly sharp glass transition. A generalized equation is proposed and utilized for configurational thermodynamic data fitting and analysis. At $X < 17$, evidence of a first-order melting transition is observed. The specific configurational enthalpy versus temperature curve displays a sudden discontinuous increase or latent heat at a well-defined glass-melting temperature, T_{gm} across the $Pt_{80-X}Cu_XP_{20}$ composition landscape. When analyzing configurational entropy, at low X, the Kauzmann temperature merges with the glass transition temperature. Below T_{gm} , ultra-fragile samples comply with the third law of thermodynamics; i.e., entropy falls and approaches that of the crystalline eutectic solid at the low-temperature limit, thereby averting the Kauzmann paradox. Configurational enthalpies of the equilibrated liquid are measured directly and relative to well-defined crystalline reference state. The $Pt_{80-X}Cu_XP_{20}$ alloy system displays a first-order melting transition from a low-temperature solid-like glass to a liquid-like phase as one progresses from a strong to a fragile metallic glass system.

2.2 Introduction

As described in the overall introduction to this thesis, there are a number of shortcomings in existing metallic glass thermodynamic theory. This chapter aims to address these shortcomings by focusing on the high- and ultra-high-fragility regime, providing an accurate thermodynamic description with a well-established reference state, proposing and utilizing a new, non-Gaussian approach to thermodynamic data fitting, and utilizing methods that provide more accurate data in the ΔT data gap of the liquid. Together, this work aims to discover what lies beneath when accurate thermodynamics are utilized.

First, a high kinetically fragile metallic glass system that retains bulk glass-forming

$Pt_{80-X}Cu_XP_{20}$ (at. %)	Fragility, m	T_g (K)	T_S (K)	T_L (K)	h_m (J/g)	GFA (mm)
$Pt_{66}Cu_{14}P_{20}$	>90	504	828.9 (1.0)	879.4 (1.0)	67.7	1.5-2
$Pt_{64}Cu_{16}P_{20}$	>90	504	827.8 (1.0)	877.5 (1.0)	68.7	3
$Pt_{62}Cu_{18}P_{20}$	>90	505	816.9 (0.5)	864.1 (0.5)	71.8	4
$Pt_{60}Cu_{20}P_{20}$	85	505	825.6 (1.0)	833.7 (1.0)	67.8	6-7
$Pt_{57}Cu_{23}P_{20}$	73	505	823.8 (0.2)	827.9 (0.2)	68.5	15
$Pt_{53}Cu_{27}P_{20}$	60	506	819.5 (0.1)	840.1 (0.1)	67.5	27

Table 2.1: $Pt_{80-X}Cu_XP_{20}$ glass system property variances with composition.[68] Heating rates utilized are noted in parenthesis in K/min.

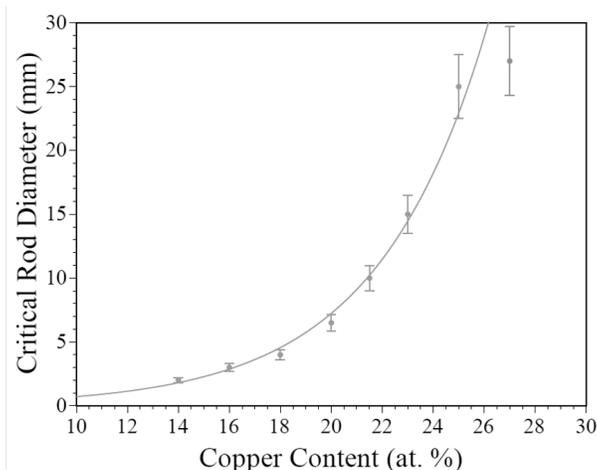


Figure 2.1: Visualization of critical rod diameter variance with copper content, X. Reproduced from Na *et al.*[68]

ability at high fragility is required. This maintained bulk glass formability will allow the application of traditional equilibrium thermodynamics and testing while supporting the high-fragility regime.

$Pt_{80-X}Cu_XP_{20}$; A Tune-able High-Fragility Bulk Glass

Due to the difficulty in casting bulk high-fragility glasses, their properties have remained predominantly unmeasured. However, in 2015, Na *et al.* at Glassmetal Technologies discovered a bulk glass-forming high-fragility BMG system. This $Pt_{80-X}Cu_XP_{20}$ system displays widely varying and tunable fragility with alloy composition while maintaining bulk glass-forming ability. The already high-fragility eutectic composition ($m = 73$ for $X = 23$) increases in fragility as the Cu content

of the alloy decreases.[10] The m reported for ultra-fragile compositions is in fact a lower bound, as the viscosity becomes highly non-Newtonian and crystallization becomes strain-rate sensitive. This makes the measurement of viscosity inaccessible at the lower Cu content when using traditional rheometric methods (TMA etc.). Table 2.1 denotes how composition adjustment dramatically alters Angell fragility, heat of fusion, and GFA with little to no change in the glass transition temperature, T_g , or melting temperatures. When $X < 17$, fragility apparently extends into the ultra-fragile $m > 90$ regime, and remarkably, GFA remains at the bulk scale (rods of several mm diameter) as visualized in Figure 2.1. This allows for use of traditional bulk calorimetric methods and traditional testing (ultrasonic testing, viscosity measurement, etc.).

Experimental Configurational Thermodynamics

The thermodynamic models and treatments described in Section 1.2 will be applied here. Combined with further underlying assumptions described in Appendix B.1, this chapter uses PEL separability to focus on configurational thermodynamics of a fragile metallic glass system.

When studying configurational components of thermodynamic functions, well-equilibrated crystal and glass states are imperative. In the PtCuP system, glass reference states are achieved through extended annealing at times several orders of magnitude greater than the α (Maxwell) configurational relaxation time; annealing of 15 hours for $X = 18 - 27$, and 3 hours for $X < 17$ due to their ultra-high fragility. These give the PtCuP alloys sufficient time to configurationally relax, thereby establishing an equilibrium distribution of inherent state configurations. This in turn justifies the application of thermodynamic relations between state variables (specific heat, entropy, enthalpy, etc.)

Establishing a well-defined crystalline reference state at fixed T is essential, for configurational enthalpies are measured as heats of crystallization and heats of fusion relative to this crystalline reference state. This method used here describes the evolution of structure energies at varying temperatures. In the PtCuP system, the crystalline eutectic solid contains three crystalline phases (Pt_7Cu , Pt_5P_2 , Cu_3P), each with distinct compositions from the liquid. This multi-phase eutectic solid acts as the well-defined thermodynamic configurational ground state in the present work.

This present work assures high-quality thermodynamic data by modifying a tradi-

tional approach. In place of commonly reported heat capacity measurements and subsequent integration to obtain enthalpy, $h(T)$, liquid enthalpy is directly measured using the crystalline reference-state approach. In traditional glass calorimetry, heat capacity is assumed to be an equilibrium property of the liquid in the absence of crystallization, but BMG heat capacities are typically measured relative to the crystal. Utilizing the present approach, liquid configurational enthalpy is reported as the heat of crystallization of the supercooled liquid state at a given temperature. This assumes that the vibrational contributions to the enthalpy of the liquid and crystal are approximately equal, and thus cancel in the vicinity of the glass transition temperature as has been experimentally demonstrated by Smith *et al.* and discussed in Chapter 1.

Appendix B.1 describes the underlying assumptions and approximations used in this work. In effect, the reported enthalpy is a direct measure of the difference in potential energy across the liquid-crystal transformation at a given T. This difference is then assumed to be purely configurational, so $h_{LX}(T) = h_C(T)$. Thus through direct measure of h_{LX} , h_c is determined. The reader is directed to Appendix B.1 for a detailed summary of how these assumptions are used to arrive at these simplifying conclusions.

Thermodynamic Theory and Analysis

Given the shortcomings of the Gaussian PEL DOS, this present work uses a more generalized approach. Equation 2.1 is introduced to describe the configurational enthalpy of the liquid. Introducing an alloy-dependent "isenthalpic" temperature, θ_h , a high-temperature enthalpy limit, $h_{LX}(\infty) = h_C(\infty)$, and an exponent n as a generalized thermodynamic fragility index:

$$h_c(T) = h_c(\infty) \left[1 - \left(\frac{\theta_h}{T} \right)^n \right]. \quad (2.1)$$

$$s_c(\phi) \propto s_c(\phi_0) - C(\phi_0 - \phi)^{\left(\frac{n+1}{n}\right)}, \quad (2.2)$$

here C is a normalization constant and ϕ_0 is the limiting value of potential energy in the high temperature limit, $T \rightarrow \infty$. Also, in this case, $n = 1$ describes the Gaussian distribution. The subsequent analysis will describe how this equation provides a new view of the Kauzmann paradox at high n (or equivalently, high m).

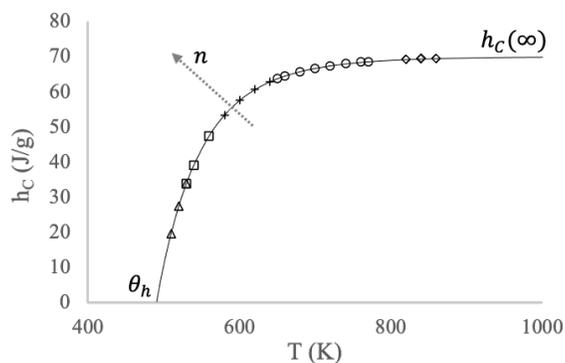


Figure 2.2: Representative h_C plot identifying $h_C(\infty)$ and θ_h terms, and depicting n -dependent curvature. Methods and respective temperature ranges are indicated by the data symbols; i.e., isothermal holds (triangle), constant heating rate (square), rapid discharge heating (plus sign), successive cyclic undercoolings (circle), melting of crystallized samples (diamond).

In effect, the experimental results of this chapter on a high-fragility BMG system demonstrate that the glass transition becomes increasingly sharper and apparently evolves toward a first-order “melting transition” in the limit of an ultra-fragile liquid. In this limit, a glass melts in much the same manner as crystals melt — with an accompanying latent heat, entropy of fusion, etc.

2.3 Methods

The overall approach records the configurational enthalpy via the heat of crystallization at various temperatures in the glass system. In order to measure the configurational enthalpy about the glass transition, methods with various thermal histories are required. Isotherms and low heating rate scans were used to measure the low-temperature heat of crystallization in the low ΔT region, and fast scans via rapid capacitive discharge heating yield mid- ΔT crystallization data. Undercoolings report high-temperature heat of crystallization, and h_C is reported at decreasing temperatures with successive undercooling cycles. All samples are reheated to the equilibrium melt following crystallization and the enthalpy of fusion is reported. These data regions are depicted in Figure 2.2 and a detailed description of each method is outlined below. Together, these methods yield the configurational enthalpy curve of the liquid relative to the enthalpy of the crystallized eutectic sample.

Sample Preparation

Samples were cast by water quenching the molten alloys in quartz tubes. The alloys are initially melted and equilibrated in a furnace at 900°C, well above the melting temperature. The sample is then quickly transferred from the furnace and quenched into a water bath. For compositions $X = 18 - 23$, rod samples were cast in 3-mm fixed-diameter quartz tubes. For $X = 14$ and 16, samples were quenched in long, tapered, drawn quartz capillaries up to 1-mm in diameter. Fluxing was not required to obtain fully amorphous samples in the PtCuP system. For all DTA runs, the end of a sample rod was made flat for good thermal contact. Each sample was cut to 30 - 60 mg for optimal signal-to-noise ratio. Samples were cleaned with 3 rinses and 1 ten-minute sonicated bath each of acetone and ethanol. Once dried, the samples were weighed and placed flat-side down in a lidded alumina pan in the DTA.

Differential Scanning Calorimetry; $h_C T$ Measurement Methods

The calorimetry work reported here was done using a calibrated Netzsch 404C F3 DTA with separate calibrations for each constant heating rate reported. A sapphire standard was used for calibration. All samples were annealed at T_g as the first step to establish a well-defined thermal history and initial sample equilibrium state. Anneal duration was dependent on fragility; $18 < X < 27$ for 15 hours, and 3 hours for $X < 17$. The error in the measured enthalpy changes for the runs was established through the measured variation of the enthalpy of fusion. Each DTA run melted the sample, and the standard deviation across these runs was determined as the instrumental error at ± 1.5 J/g.

Isothermal Holds

After annealing at T_g , samples were heated at 2 K/min to a range of temperatures above T_g in the ΔT region and held isothermally at a fixed T until crystallization occurred. Post crystallization, the samples were subsequently heated at 10 K/m through the melting transition. Isothermal hold temperatures ranged 232 to 252°C or 505 to 525K. Specific enthalpies of crystallization and fusion were recorded and added to the $h_C(T)$ plots. Isothermal runs minimize thermal lag effects in the calorimeter, allowing the instrument to reach stable steady-state conditions with a well-defined signal baseline. In turn, this permits a very consistent and most accurate determination of the heat of crystallization. However, due to the slow heating rate to approach the isothermal hold temperatures and the finite time required to achieve

steady-state, accurate heat of crystallization data above 252°C or 525K could not be obtained since crystallization intervenes before steady-state is achieved in the DTA. Thus, to measure the heat of crystallization further into the ΔT region, one must switch from the isothermal protocol to a constant heating rate protocol following initial annealing at T_g .

Constant Heating Rate

After the annealing step, samples are heated at a constant heating rate through crystallization and melting using a large range of rates, including 0.1, 0.5, 1.5, 3, 5, 8, 10, 15, and 20 K/min. This broad range assured the transition from isothermal crystallization conditions to constant heating conditions was well explored, and the heat of crystallization (or equivalently the configurational enthalpies) across a range of temperatures was recorded. The shift in crystallization onset with temperature is in part due to the instrumental lag (transient instrumental response) at higher heating rates. Heating rates at and below 5 K/min are preferred for better sample equilibration and reduced thermal lag within each run. The lower the heating rate, the sharper the DTA time and temperature resolution achieved for the heat of crystallization. Calibration runs of the melting transition of Sn at various heating rates were used to correct for instrumental thermal lag effects. Tin's melting point at 231.9°C is optimally located very near the PtCuP T_g of $\sim 230^\circ\text{C}$, thereby providing an optimal correction for transient instrumental effects. The correction runs are included in Appendix B.3. In general, 20 K/min heating rates are commonly used in DSC and DTA studies reported in literature, but thermal lag effects are seldom accounted for. By directly accounting for transient instrumental broadening and temperature shift of the exothermic crystallization DTA signal, we are able to improve the temperature resolution in our $h_{LX}(T)$ measurements. Basically, we more precisely determine the sample temperature during the liquid-crystal transformation.

Cyclic Undercooling

As-cast samples are cycled repeatedly (heating and cooling) from below T_g through crystallization and melting ($T_m + 150\text{K}$) at 5 K/min in the DTA. The number of cycle steps is limited only by the number of programmable steps in the DTA. This method allows for the collection of crystallization data over a wide range of temperatures in the undercooled region. Successive undercoolings yield the crystallization event at progressively lower and lower temperatures, thereby enabling collection of heat of

crystallization data in the upper range of the ΔT region of the h_C curve.

Melting

Heating through melting of the crystallized sample was carried out after each crystallization run to assure a complete liquid-crystal transformation had occurred. Any additional heat release events were investigated for structural differences via XRD. The heat of fusion was determined for each sample following each crystallization transformation.

Rapid Capacitive Discharge Heating

Rapid capacitive discharge heating (RDH) was used to measure data in the mid- ΔT region. The system uses ohmic dissipation with 15-kJ capacitive discharge heating on rod samples 3-cm in length and ranging from 3 to 5-mm in diameter. Samples were uniformly heated at heating rates up to $\sim 10^5$ K/s by fully discharging a capacitor bank from various charging voltages to vary the energy deposited in the sample rod. The sample is clamped between two copper electrodes. Temperature was measured with the Impac series 5 non-contact high-speed pyrometer with a 5 μ s time resolution. A FLIR SC-4000 infrared camera was combined with the RDH system for infrared images of coupled eutectic growth (see Figure 2.5). The infrared camera functions with 256,000 pixels and frame rates up 1,300 frames/s.

Data Analysis; $h(T)$

For each of the methods listed above, the heat flow signal is recorded as a function of temperature and or time (for isothermal segments). Configurational enthalpy is calculated as the area beneath the exothermic crystallization curve and the enthalpy of melting is calculated as area under the endothermic melting transition.

Additional Methods

Additional methods that provided supporting information for the thermal analysis are included here. Viscosity was measured via Beam Bending in a Perkin-Elmer Thermo Mechanical Analyzer. X-ray diffraction scans were completed with a Bruker D2 Phaser diffractometer. The shear modulus was measured using ultrasonic transducers in the pulse-echo configuration. 25-MHz quartz transducers were used to determine the shear sound velocities on 3-mm diameter rods. Density was measured via wet/dry mass measurement in the Archimedes method.

2.4 Results and Discussion

While many properties of the PtCuP alloy family are detailed in Table 2.1, the supercooled liquid must first be verified to be in metastable configurational equilibrium in order to apply equilibrium thermodynamic relationships in the analysis of data. Configurational relaxation takes place with a characteristic time scale given by the Maxwell relaxation time of the liquid. In turn, this can be determined from the viscosity of the liquid along with knowledge of the liquid high-frequency shear modulus. For $X = 23$, at T_g , time to crystallization onset is observed as $t_{LX} > 10^6$ s (~ 1 wk). This establishes the samples as metastable liquids, where the initial anneal times are sufficiently short to avoid nucleation and growth of crystalline phases. Before subjecting samples to thermal analysis, the achieved metastable equilibrium state must be verified further. Viscosity data are used to assess the extent of liquid configurational relaxation prior to crystallization. These data, in combination with the shear modulus, were used to estimate the Maxwell configurational relaxation time for the undercooled liquid, $\tau_\alpha = \tau_M = \eta(T)/G$, with $G \sim 32$ GPa measured ultrasonically. Initial isothermal holds reported crystallization peak times, t_{peak} . The $X = 23$ data for t_{peak} and τ_α are illustrated in Figure 2.3a, where they are the top and bottom curves, respectively. When compared, the ratio of t_{peak} and τ_α quantifies the extent of liquid relaxation toward metastable configurational equilibrium prior to crystallization. With this ratio ranging from 10^3 to 10^6 for $X = 23$ and 20, it indicates that h_{LX} is representative of a configurationally relaxed undercooled liquid in metastable equilibrium prior to the onset of crystallization. It follows that the measured heat of crystallization is characteristic of the transformation of an equilibrium liquid to an equilibrium crystalline sample. This knowledge is applied to the remainder of the PtCuP glass system.

Along with an established metastable configurational equilibrium, the crystallization behavior of this system is important to defining a reference state for configurational thermodynamics. Initial observation of crystallization in the PtCuP system reports a sharp exothermic peak with rapid onset and decay. The peak shape is uniform across isothermal runs as plotted on a logarithmic time scale when normalized to peak height and peak time (Figure 2.3b). The crystallization event completes in a time, Δt_{LX} , much shorter than the preceding incubation period; $\Delta t_{LX} \ll t_{LX}$. The peak and transformation times follow simple scaling behavior, which implies a single crystallization event/mechanism. This is further verified by a pyrometer visualization of Rapid Capacitive Discharge where a single crystallization front is recorded. See the discussion accompanying Figure 2.5.

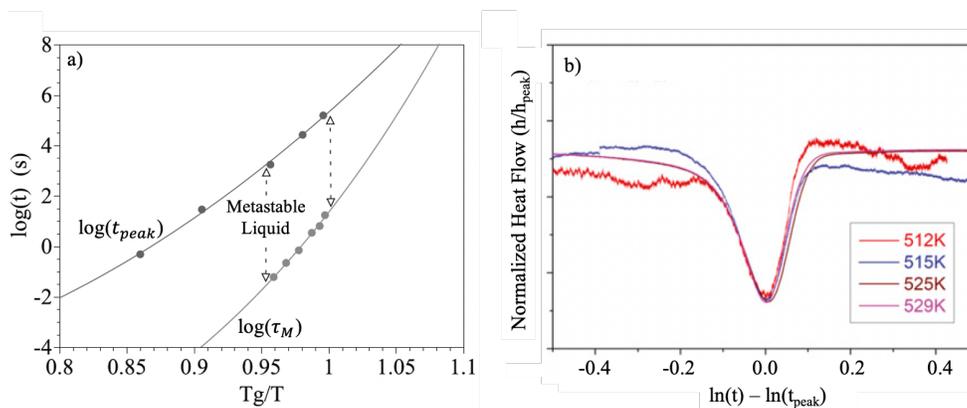


Figure 2.3: t_{peak} to $\tau_\alpha = \tau_M$ defined metastable liquid region (a), and normalized DTA scans displaying uniform peak shape (b). Reprinted with permission from [68].

Further evidence of a single sharp crystallization event comes from XRD analysis. As described in the Methods section, each run underwent multi-hour anneals, crystallization (isothermally or under constant heating rates), and then reheating and melting. XRD scans were carried out on the samples after each thermodynamic step and thermodynamic event. At slower heating rates, some samples expressed a second but smaller exothermic peak during reheating between the initial large crystallization event and melting. XRD results indicated a fully amorphous sample up to the initial crystallization event, and revealed no new crystalline diffraction peaks after the smaller second event (Figure 2.4). Thus the crystallization event at 240°C describes full crystallization. Further, with XRD showing no change in structure after the smaller second exothermic peak, it is believed that this excess heat release is due to coarsening of the microstructure produced by the primary/initial event.

Now that the equilibrium nature of the metastable liquid is validated and crystallization behavior understood, the enthalpy measurements from each method take focus. First, particular notes on data collection are described before greater trends are discussed across compositions and fragility. As discussed above, the isothermal holds have a clean sharp peak, but present a secondary peak between 320 – 340°C. This second peak is also observed in slow constant heating rate scans. However, this second peak merged with the primary peak for heating rates above 1 K/min. When present, the excess heat release peak is assumed due to relaxation or coarsening as was done for the isotherms. And in both cases, the second Δh_C was added to the first to equal the reported h_C . The h_{LX} onset temperature data are adjusted according to the Sn melting corrections in Appendix B.3 and the raw data are included in

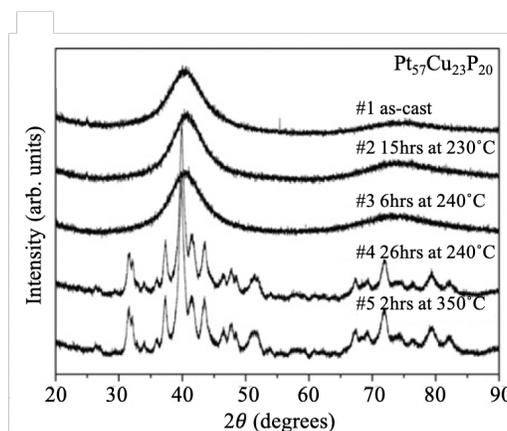


Figure 2.4: XRD post each thermodynamic step and transition for $X = 23$. Reprinted with permission from [68].

Appendix B.4. No other heat release events are detected in other scan segments. The isothermal scan and constant heating rate data compose the lower-temperature data within the ΔT region just above the glass transition.

A third set of DTA scans include cyclic undercooling data. Here, the as-cast samples underwent forty heating/cooling cycles from 200 to 900°C at 10 K/min. Undercooling increased with successive cool-reheat cycles. This deepening of undercooling is assumed due to the dissolution of heterogeneous crystal nucleants through cycled overheating of the melt. Maximum undercooling was achieved to 365°C, which is $\sim 180^\circ\text{C}$ below the eutectic temperature, T_E , taken as the average between the solidus and liquidus temperatures. The undercooling data fill in the h_C curve from just above the nucleation nose to $\sim 50^\circ\text{C}$ below T_E .

Melting data were collected for every scan during reheating, and describe the configurational enthalpy at the melting point, $h_C(T_E)$. These are the highest-temperature data on the h_C plots.

Measurements via rapid capacitive discharge contribute $h_{LX}(T)$ data to the mid- ΔT region. Figure 2.5a plots the T vs. t data. It visualizes the ultrafast heating to 350°C, configurational relaxation and stabilization at $\sim 312^\circ\text{C}$, and rapid recalescence. Recalescence achieves 505°C which is below but near T_E . The ultrafast pyrometer data (Figure 2.5b) reveal a single crystallization event via coupled eutectic growth. The singular growth front proceeds at $\sim 1.5\text{-cm/s}$. This very high growth rate suggests short-range chemical order for the crystal phases may already present in the liquid, therefore mitigating the need for chemical partitioning along the advancing

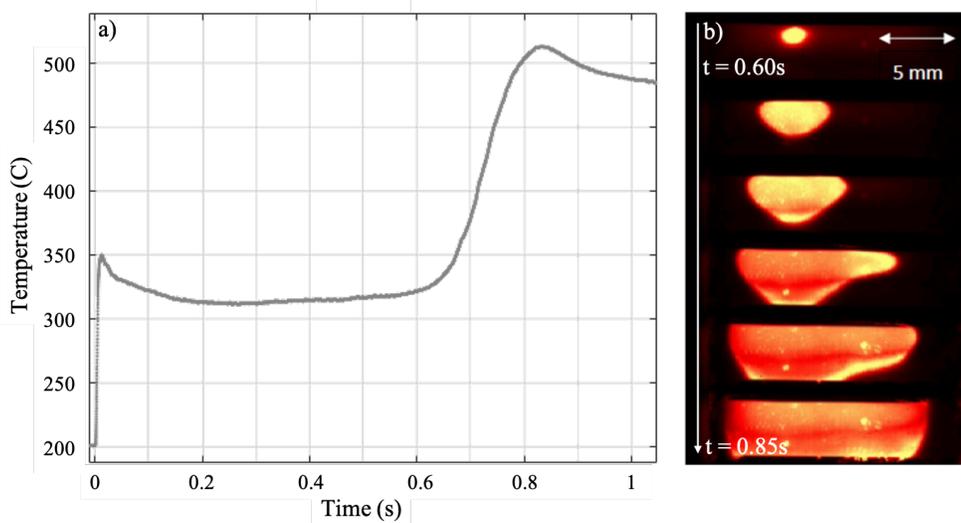


Figure 2.5: Rapid heating profile of the $X = 20$ sample. a) Temperature vs. Time profile shows rapid heating on recalescence. b) Ultrafast pyrometer from $t = 0.6$ -- 0.85 s. Reproduced with permission from [68].

crystallization front, and further explains the small Δt_{LX} . The temperature increase on recalescence was used to estimate the heat release as 52 J/g and was reported on the h_C plot along with the other calorimetric data.

With the data collected from the aforementioned methods, $h_C(T)$ plots are constructed first for $18 < X < 27$, while a further discussion will be made for $X < 17$. Figure 2.6a-d compiles the configurational enthalpy data for these compositions. These data are fit with Equation 2.1 (99.4% correlation) with fitting parameters listed in Table 2.2. From Figure 2.6a-d, the curvature of h_C increases from the fragility index, n , rising along with increasing Angell fragility, m . In $X = 18$, the isotherm and constant heating rate data report different behaviors in the low-temperature region of the h_C curve. The two data sets have different slopes, but are more vertical than that for the stronger, higher X glasses. In fact, the temperature-corrected constant heating rate data suggest a vertical jump at 551K , indicative of a potential latent heat. This separation from the low T h_C data in $X = 20 - 27$ marks the higher fragility samples as worth greater inquiry. This will be included in the discussion on $X = 14$ and 16 samples.

For better comparison, the $18 < X < 27$ data were plotted on axes normalized by the isenthalpic temperature (θ_h) and the high temperature limit of enthalpy ($h_C(\infty)$). Figure 2.7 collects the Pt alloy data on one plot and highlights the

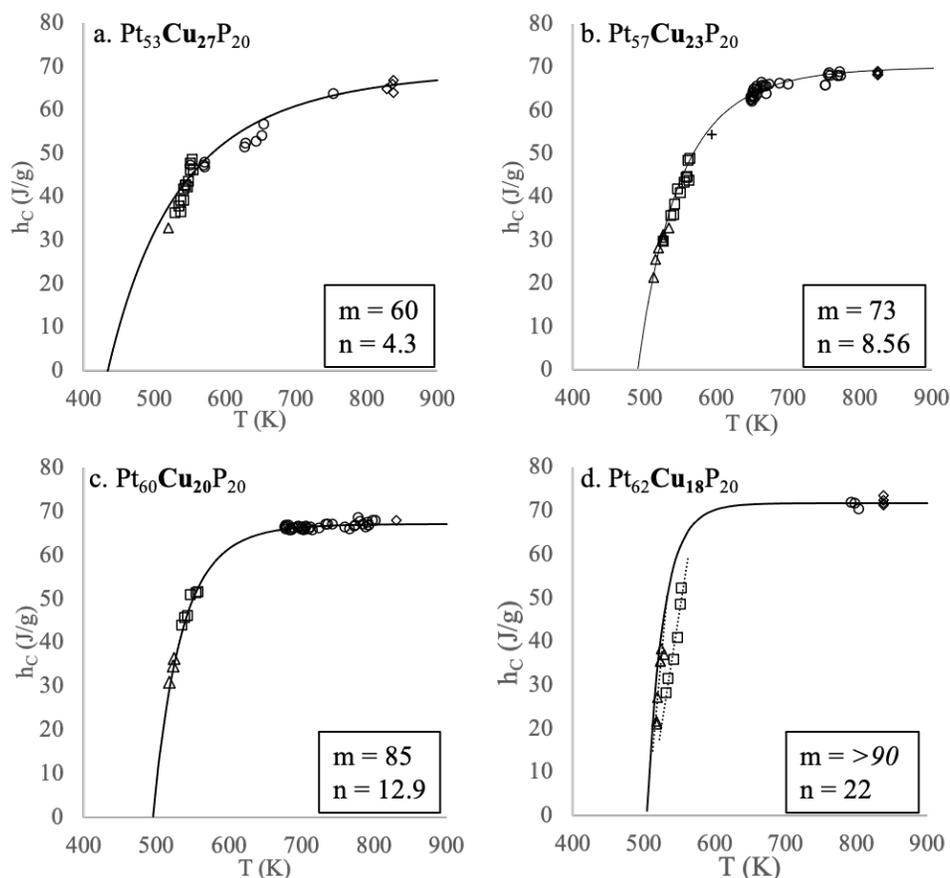


Figure 2.6: h_C data plotted per method and composition. Method key matches that of Figure 2.2. Reproduced with permission from [68].

$Pt_{80-x}Cu_xP_{20}$ (at. %)	$H_c(\infty)$		n	m	T_K^* (K)	$\frac{h_R}{h_C(\infty)}$
	(J/g)	θ_h (K)				
$Pt_{66}Cu_{14}P_{20}$	67.9	561.1*	-19.2*	>90	562.1*	0.383
$Pt_{64}Cu_{16}P_{20}$	68.5	560.5*	-28.3*	>90	560.7*	0.360
$Pt_{62}Cu_{18}P_{20}$	72.4	508.3	25.7	>90	517.4	0.360
$Pt_{60}Cu_{20}P_{20}$	68.3	492.2	13.3	85	511.4	0.341
$Pt_{57}Cu_{23}P_{20}$	70.2	484.8	8.36	73	505.5	0.334
$Pt_{53}Cu_{27}P_{20}$	69.9	433.6	4.3	60	472 ± 10	0.266

Table 2.2: Fitting parameters for configurational enthalpy (Equation 2.1) curves in Figure 2.6a-d. Reproduced with permission from [68].

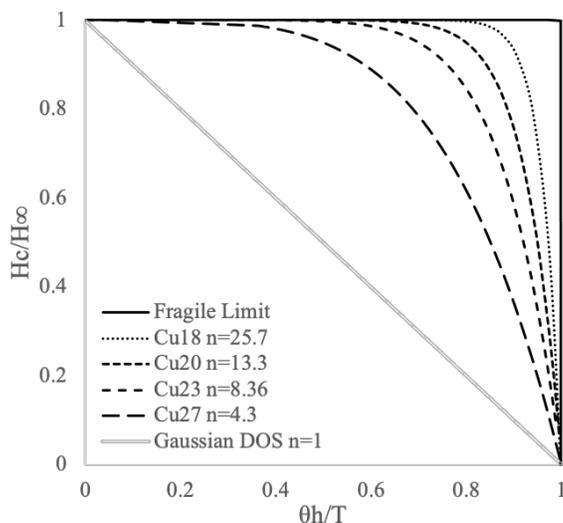


Figure 2.7: Fully normalized h_C plot for composition and n comparison. Method key matches that of Figure 2.2. Reproduced with permission from [68].

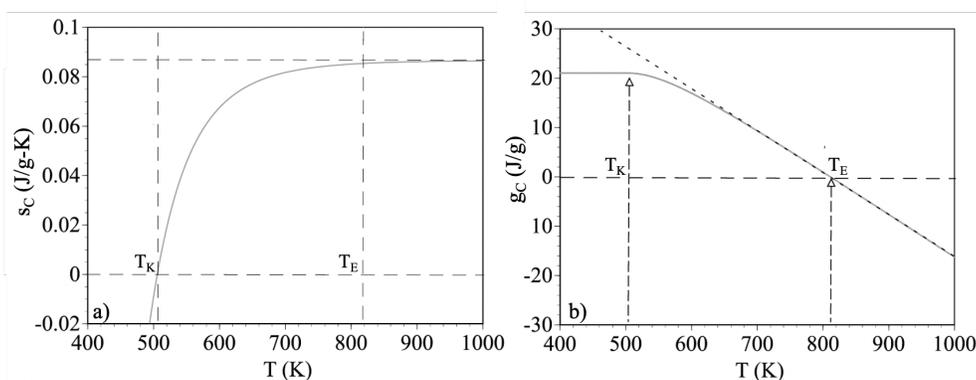


Figure 2.8: Specific configurational entropy (a) and specific configurational Gibbs free energy for $Pt_{57}Cu_{23}P_{20}$. Reprinted with permission from [68].

increase in curvature from n , with increasing fragility, m . The plotted n 's for PtCuP system increase from $n = 4.3$ and are included in the figure key. Projected at higher fragilities is the fragile limit; the case in which n goes to infinity. In this case, the configurational enthalpy approaches a heavy-side step function and implies possible first-order transition behavior. For context, recall the Gaussian PEL enthalpy Equation 2.1 is described by $n = 1$. The Gaussian enthalpy is superimposed on Figure 2.7 and demonstrates, as expected, that the experimental data deviate greatly from this model. This further demonstrates the Gaussian model inaccuracy and the need for an accurate equation to describe the measured thermodynamics. With 99.8% correlation, Equation 2.1 is a prominent contender.

With the now complete specific configurational enthalpy curves and the excellent analytic fits provided by Equation 2.1, the enthalpy can be integrated to achieve configurational entropy and free energy. The fit of Equation 2.1 to the thermodynamic data was used to analytically compute the specific configurational entropy, $s_C(T)$, and specific configurational Gibbs free energy $g_C(T)$. By integration, the expression of $s_C(T)$ is:

$$s_C(T) = \Delta s_F(T_E) + \int_{T_E}^T \frac{h_C(\infty)}{n} \theta_h^n dT T^{n+2} = \Delta s_F(T_E) - \frac{nh_C(\infty)\theta_h^n}{n+1} \left(\frac{1}{T^{n+1}} \right) \Bigg|_{T_E}^T \quad (2.3)$$

where the integration constant is the measured entropy of fusion $\Delta s_F(T_E)$ at the eutectic temperature, T_E . From the configurational entropy, the Kauzmann temperature, T_K , is determined using $s_C(T_K) = 0$ where Δs_F is reported in normalized dimensionless units of $h_C(\infty)/\theta_h$. Figure 2.8a reports the specific configurational entropy for X = 23.

$$T_K = \frac{T_E}{\left[1 + \left(\frac{n+1}{n} \Delta s_F \left(\frac{T_E}{\theta_h} \right)^{n+1} \right) \right]^{\frac{1}{n+1}}}. \quad (2.4)$$

For X = 23, $T_K = 505.5\text{K}$, very close to the calorimetric onset T_g of 505K. Further, it is close to the rheologic T_g onset of 501.5K. To this end, the experimentally defined T_K is effectively indistinguishable from the thermodynamic and rheological glass transition temperatures. The remaining Kauzmann temperatures for the other compositions are listed in Table 2.2 and can be compared with the calorimetric glass transition temperatures reported in Table 2.1.

To attain the Gibbs free energy, we recall that at ambient pressures, the "Pv" term can be ignored (compared with h_C and T_s terms). Therefore $g_C(T) \sim h_C(T) - Ts_C(T)$. We assume at T_K the glass configurationally freezes, where below T_K , $s_C(T) = 0$, and $g_C(T) = h_C(T_K)$. From these fits, below T_K , entropy becomes negative (subensemble), suggesting the system runs out of configurational states when frozen at T_K . In Figure 2.8b, $g_C(T)$ remains linear with respect to T down to deep undercooling. This suggests configurational freezing sets in only at very deep liquid undercooling and agrees with the Turnbull approximation for modest undercooling.[8, 69]

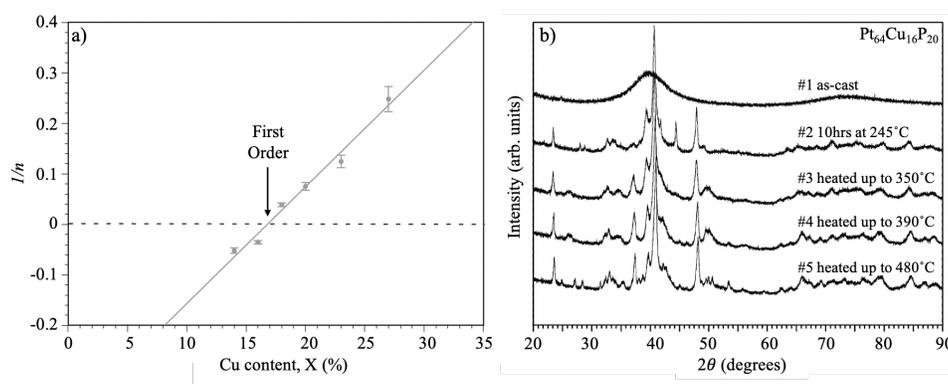


Figure 2.9: Variation of effective glass transition width, $1/n$, with copper content (atomic %) (a). XRD plots for $X = 16$ (b). Reprinted with permission from [68].

At T_K , the entropy and enthalpy have different behaviors. While the configurational entropy reaches zero at T_K , the configurational enthalpy remains finite. This leaves a residual enthalpy, $h_R = h_C(T_K)$, above that of the crystallized eutectic reference state. This residual enthalpy is calculated relative to the high temperature limit of enthalpy and reported in Table 2.2 under $h_R/h_C(\infty)$. h_R represents the heat of crystallization of a fully ordered ideal glass at T_K , where the configurational enthalpy of the ideal glass lies T_R above that of the crystalline state.

The analysis for $18 < X < 27$ has revealed promising results for configurational freezing and a residual enthalpy, but when comparing the fitting parameters in Table 2.2 to copper content, X , a separation of character occurs at $X \sim 17$. With n as the thermodynamic fragility parameter of Equation 2.1, $1/n$ represents the relative glass transition (half) width. When $1/n$ is plotted against copper content, X , Figure 2.9a uses a simple linear fit that suggest that n diverges at $X \sim 17$. This divergence implies the glass transition passes through a critical point and becomes a first-order freezing transition at $X = 17$, and thus makes the lower copper content samples of particular interest.

When compiling the configurational enthalpy data, the Sn heating-rate onset temperature corrections were utilized. The data for $X = 14, 16$ from the various methods are summarized in Figure 2.10. When T_C is temperature corrected for the heating rate shift for $X = 14$ and 16 , a clear vertical step emerges. This discontinuous step is a latent heat and indicative of a first-order glass-melting transition. The onset temperature is defined as T_{gm} , effectively the melting temperature of the low-temperature “solid like” glass. For $X = 14$, $T_{gm} = 533\text{K}$, $\sim 30\text{ K}$ above the nominal calorimetric onset T_g , and the latent heat of the transition is determined to be ~ 27

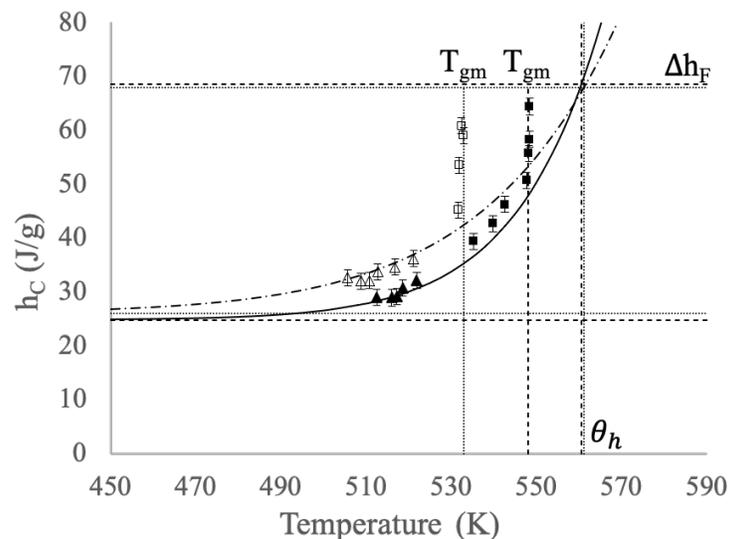


Figure 2.10: Specific configurational enthalpy for $X = 14$ and 16 . $X = 14$ and 16 data and limits plotted with dot-dash and solid lines, and dotted and dashed lines, respectively. Reproduced with permission from [68].

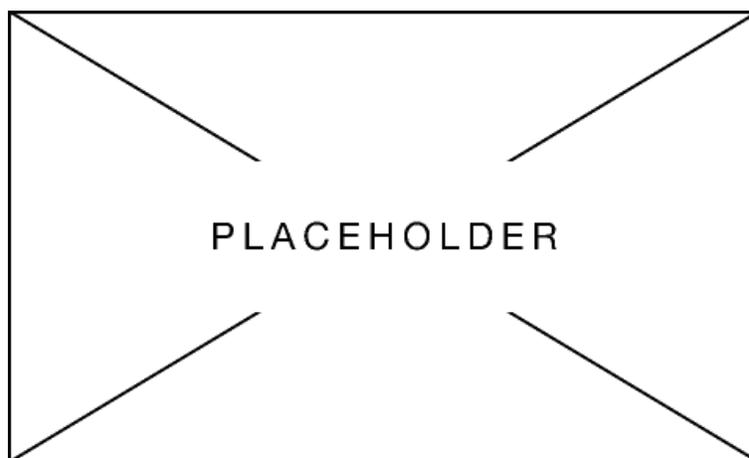


Figure 2.11: [This figure and accompanying analysis is embargoed pending publication.]

J/g. For composition $X = 16$, a slightly smaller step discontinuity of ~ 20 J/g occurs at a somewhat higher $T_{gm} = 548$ K. Both curves display behavior of a latent heat and a first-order glass-liquid melting transition.

[This analysis is embargoed pending publication.]

Returning to focus on $X = 14$ and 16 , in addition to the enthalpy jump at T_{gm} , Figure 2.10 shows the opposite curvature at low temperatures compared to the $18 < X <$

27 compositions. This curvature change makes the current form of Equation 2.1 no longer appropriate. Fortunately, Equation 2.1 can be modified with the gained knowledge of the additive residual enthalpy and put into a power law form;

$$\frac{(h_C(T) - h_R)}{(h_C(\infty) - h_R)} = \left(\frac{T}{\theta_h}\right)^n. \quad (2.5)$$

This new equation describes the approach to melting of the glass from below the first-order transition and intersects with the enthalpy of fusion at T_{gm} . With this modified equation, the fitting parameters have shifted as well. θ_h now represents the temperature where the low-temperature $h_C(T)$ curve crosses $h_C(\infty)$, or equivalently (when n is very large) where $h_C(T)$ for the low-temperature solid-like glass crosses the enthalpy of fusion of the eutectic crystalline solid. The n parameter now has a negative sign, which describes the glass freezing. Finally, $h_C(T)$ uses the ideal glass h_R as the natural zero for this adjusted glass enthalpy. With increasing n , Equation 2.5 approaches a heaviside step function from below θ_h . In Figure 2.10, X = 14 and 16 are fitted with the results $n = -19.2$ and -29.2 , respectively. The fitting parameters are included in Table 2.2.

The curves in Figure 2.10 predominantly fit isothermal scan data for the ultra-fragile samples below T_{gm} . For X = 14 and 16, the residual glass enthalpies approach h_R of ~ 26.0 J/g and 24.5 J/g, respectively. The temperature dependence of h_C below T_{gm} suggests that the equilibrium solid-like glass is a configurationally excited state. However, the potential of slow kinetics limiting relaxation and equilibration of the glass below T_{gm} is unlikely. Particularly since the data were collected under isothermal conditions with anneal times exceeding the Maxwell relaxation time by orders of magnitude. Therefore, with assuming the data represent a well-equilibrated glass, Equation 2.5 can be used to compute the configurational entropy.

Using the fits of Equation 2.5, the entropy is calculated by integration of $\Delta h/T$ from low-temperature where $s_C = 0$ to temperature T_K^* . T_K^* describes an "inverse" Kauzmann temperature. In effect, this temperature is where the glass configurational entropy extrapolates to the entropy of fusion of the crystalline eutectic alloy, i.e., where $s_C(T_K^*) = \Delta s_F$. The configurational entropy for X = 14 and 16 is plotted in Figure 2.12. The equation for T_K^* is summarized as follows:

$$T_K^* = \theta_h \left[\frac{(n-1)(h_C(\infty) - h_R)\theta_h}{nh_C(\infty)T_E} \right]^{1/(n-1)}. \quad (2.6)$$

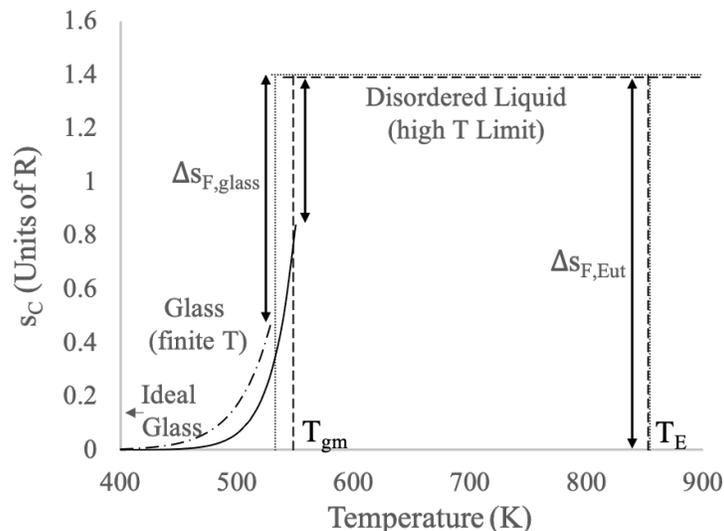


Figure 2.12: Specific configurational entropy for $X = 14$ and 16 . $X = 14$ and 16 data and limits plotted with dot-dash and solid lines, and dotted and dashed lines, respectively. Reproduced with permission from [68].

T_K^* functions as an upper bound for the glass-melting temperature and is slightly lower for $X = 14$ than for $X = 16$, implying a more restrictive upper bound on the highest fragility sample tested.

For the overall specific configurational entropy as a function of T , a piece-wise continuous function is constructed as shown in Figure 2.12. The piece-wise plot combines the fits of measured latent heat of glass-melting at T_{gm} and the entropy of fusion of the crystalline eutectic. The figure shows $s_C(T)$ in units of the gas constant, R , for $X = 14$ and 16 . Within the above assumptions, for $X = 14$, the configurational entropy at T_{gm} is 0.0308 J/gK or $0.533 R$. Equation 2.5 provides a description of glass entropy from $T = 0\text{K}$ to T_{gm} . With the curvature present in the ultra-fragile $X = 14$ and 16 samples, the equilibrium glass configurational entropy never becomes negative, but rapidly approaches that of the crystallized eutectic solid as T falls below T_{gm} . For the solid-like glass, the configurational entropy, $s_C(T)$, at $T = 0\text{K}$ vanishes within uncertainty of $\sim \pm 0.03R$. Thus, within the stated uncertainties, the Kauzmann paradox is resolved where $s_C(T)$ obeys the third law of thermodynamics for the solid-like glass phase. Effectively, the solid-like glass behaves much like a crystalline solid but with a smaller heat of formation for configurational excitations per Equation 2.5.

It is important to recall that phonon/vibrational contributions to the total entropy have

been excluded from this analysis (as these are assumed to be roughly equal for both the glass and crystalline states in the temperature range of interest). While crystallization data technically include contributions arising from anharmonic differences between the glass and crystalline states, they are apparently small by comparison to configurational differences. This is understood because anharmonicity displays a " T^2 " contribution to the enthalpy of crystallization, but the high n values are in stark contrast to this potential contribution. Therefore, Equation 2.5 and high n values strongly suggest that these anharmonic contributions are relatively small and realistic to exclude. Therefore configurational degrees of freedom are expected to dominate the temperature dependence of specific enthalpy below T_{gm} .

In effect, the ordered glass can be viewed as a configurationally ordered solid, but with an infinite unit cell. It makes sense that this configurationally ordered glass has a distinct configurational ground state enthalpy, h_R , differing from that of the eutectic crystalline solid. As discussed in Section 1.4, allotropes and polymorphic crystals have ordered phases with phase-specific ground state energies. This is a reasonable extension to a fully ordered solid-like ideal glass state as well.

2.5 Summary and Conclusion

The $Pt_{80-X}Cu_XP_{20}$ system was a key part of this thesis research, and demonstrates several prominent results. The homogeneous liquid exerts a single sharp crystallization event following coupled eutectic growth. This crystallization produces a well-defined crystalline reference state and allows for a direct and accurate measure of the liquid enthalpy relative to that reference state. Before testing, the $Pt_{80-X}Cu_XP_{20}$ system achieves a verified configurationally relaxed metastable state. The incubation time before crystallization, t_{LX} , exceeds the Maxwell relaxation time, $\tau_\alpha = \tau_M$ by several orders of magnitude, thus indicating the required metastable equilibrium of the liquid is achieved before crystallization onset. Together, these features allow an accurate assessment of the metastable equilibrium configurational enthalpy of the liquid in reference to the crystalline eutectic solid. These features justify the application of classical thermodynamics to compute the state functions of the liquid phase.

The thermodynamic functions obtained from this work revealed the specific configurational enthalpy departs drastically from the $1/T$ temperature dependence expected in the PEL Gaussian model. In actuality, $n = 1$ represents the Gaussian Landscape model in Equation 2.1, but the magnitude of n is much larger for the reported

high-fragility and ultra-high fragility PtCuP samples. With Equation 2.1 and its modification to Equation 2.5, this implies the density of inherent states approaches a simple exponential behavior for $W(\phi)$ and is not Gaussian (see discussion in Chapter 1). With Equation 2.1, with increasing n , we see a divergence in heat capacity at $T = \theta_n$. Similarly, the glass transition approaches first-order melting behavior as $1/n$ approaches zero. For $X = 14$ and 16 , one observes clear evidence of a latent heat and first-order melting behavior of a solid-like glass to a fluid-like state. Equation 2.5 accounts for the residual enthalpy as one approaches the melt transition at T_{gm} from below. Within measurement error and the assumptions of this work, a discontinuous enthalpy (latent heat) is observed at a well-defined temperature T_{gm} for $X = 14$ and 16 compositions. This provides distinct evidence of a first-order melt transition of this ordered ideal glass to a disordered liquid state where the liquid appears to be in its high-temperature limit just above T_{gm} . For configurational entropy, the solid-like glass follows a power law up to T_{gm} , but approaches zero (within error) as temperature approaches zero. Thus, within the error and the assumptions of this work, the ultra-fragile liquid averts the Kauzmann paradox through a first-order freezing transition, and the configurational entropy obeys the third law of thermodynamics below the glass freezing temperature.

Ultra-fragile glasses demonstrate a distinct latent heat and glass-melting transition temperature where a solid-like glass melts to a liquid-like phase. It is important to note that both of these phases are non-crystalline (Figure 2.4). **[This conclusion is embargoed pending publication.]**

These claims of a configurationally ordered glass are supported by Molecular Dynamics (MD) results by Berthier *et al.* and An *et al.* Berthier *et al.* have reported ultrastable (configurationally relaxed) atomic glasses that exhibit first-order melting on rapid heating through T_g . [70, 71, 72] These glasses are prepared by simulation of layered atomic deposition onto heated substrates (near T_g). This allows for a degree of configurational relaxation not thought possible on cooling of a monolithic liquid. [70, 71] Berthier's MD simulations showed a first-order melting front propagation similar to direct melting of crystals and similar to the results reported here for the PtCuP system. The MD analysis concluded the first-order melting arose from the highly-ordered low configurational enthalpy ultrastable glass. It is believed that the present work observes a similar highly-ordered low configurational enthalpy/entropy ultrastable glass in the ultra-fragile $Pt_{80-X}Cu_XP_{20}$ samples.

Further, the findings in this work are connected to the metastable structural and

energetic intermediate G-phase glass state in An *et al.*'s works described in Section 1.4. It is believed the PtCuP metastable configurational equilibrium solid-like glass state is equivalent to the G-glass phase glass state reported from the MD simulations, while the fluid-like phase in the $X = 14, 16$ case is equivalent to the L-phase glass/liquid identified by An *et al.* The presence of the glass-melting transition provides a natural starting point to explore mechanical and other characteristic properties on either side of the first-order glass-melting transition. Attempts to follow this line of investigation are reported in the next chapter where the possible connection to the G-glass (and L-glass) is further strengthened.

*Chapter 3*CHARACTERIZATION OF THE SECONDARY GLASS PHASE
IN ULTRA-FRAGILE $Pt_{80-x}Cu_xP_{20}$ BULK METALLIC GLASS

[This chapter is embargoed pending publication.]

*Chapter 4*EMBRITTLMENT TRANSITION IN NI-BASED BULK
METALLIC GLASS AS EVIDENCE OF THE G-PHASE GLASS

[This chapter is embargoed pending publication.]

CONCLUDING REMARKS

5.1 Conclusions

The three final chapters presented in the thesis draw direct links to the second glass phase described in Chapter 1, Section 1.4. The combined works establish experimental evidence for two distinct glassy phases across the spectrum of strong to high- and ultra-high fragility metallic glass forming liquids.

Given that the secondary glass was first identified computationally in ultra-high fragility Ag and binary AgCu and CuZr, experiments initially pursued the same high fragility regime. Configurational thermodynamics on the $Pt_{80-x}Cu_xP_{20}$ system (Chapter 2) employs accurate direct measurements of the anneal-equilibrated liquid configurational enthalpy as a function of temperature. This reveals an apparent first-order glass-melting transition with discontinuous enthalpy and entropy changes at the phase boundary, T_{gm} . **[This conclusion is embargoed pending publication.]** Further, the utilization of a new DOS approach to describe configurational entropy and accurate data accumulation methods present a configurational entropy that vanishes in the low-temperature limit, averting the Kauzmann paradox.

With the configurational thermodynamics approach employed in Chapter 2 revealing the second glass phase behavior in annealed samples, mechanical, structure, and thermodynamic approaches were utilized to reveal distinct physical characteristics between the primary and secondary glasses (Chapter 3). **[This conclusion is embargoed pending publication.]** These two studies on the high-fragility to ultra-fragile PtCuP alloys provide a promising multi-faceted foundation for the experimental observation of two distinct glass phases.

Finally, the Ni208 study on a hypothesized second glass phase-induced embrittlement transition extends the discussion to the kinetically strong glass forming liquid regime (Chapter 4). **[This conclusion is embargoed pending publication.]**

The thesis presents direct experimental evidence of a novel glass-melting transition, and presents a new solid-like glass phase. The evidence of the second glass phase extends from strong to ultra-fragile glasses, and validates the initial computational discovery. Paired with further computational and experimental studies, the second

glass phase is further predicted across traditional glass systems.

5.2 Summary of Outcomes

These results were achieved following the motivations outlined in Section 1.5 (indicated by the numbers in parentheses). The PtCuP system of Chapters 2 and 3 provided a high-fragility and ultra-fragile glass system for the previously unexplored regime (1). A direct calorimetry study of configurational thermodynamics was applied with a well-equilibrated glassy state (2), a new analytic expression to better represent the configurational enthalpy data was introduced (3), and an apparent glass-melting transition was revealed through improved accuracy of calorimetric data. **[This outcome summary is embargoed pending publication.]** These motivations yielded both the glass-melting transition and a resolution to the Kauzmann paradox at ultra-high fragility. **[This outcome summary is embargoed pending publication.]** While these motivations proved very fruitful for this work, there remain further questions to address.

5.3 Future Work

The combined works of this thesis provide experimental evidence and support for the secondary glass phase. Specific details of An *et al.* and Shen *et al.* were emphasized and verified in these studies (i.e., hardness, latent heat and melting transition, heterogeneous structure, and composition equivalence). But in addition to these addressed and verified G-phase characteristics, An *et al.* also investigated the L-G transition through the lens of rigidity. They demonstrate that the L-G transition corresponds to the emergence of elastic rigidity from determining the shear modulus and the persistence of stress fields of each phase.[73] With an onset of rigidity from the L to G phase, the melting transition (G to L) is described as a loss of elastic rigidity. This is related to rigidity catastrophe described by the Born melting criterion as discussed in Section 1.4.

A future study is proposed to probe the rigidity loss on G-phase melting. The shear modulus can be measured with respect to temperature using ultrasonic methods and *in-situ* transducers. Following the methods utilized by Mary-Laura Lind in her 2008 Ph.D. dissertation, the shear modulus can be mapped versus temperature and time. With increasing temperature on as-cast and annealed samples, the decay of the shear modulus can be investigated. Further, observation of the evolution of the heterogeneous G-phase structure over temperature in high-resolution TEM, or using high-speed synchrotron X-ray methods would likewise shed valuable light on

the structure and structural transformation that accompanies the G-glass-melting transition.

[This future work is embargoed pending publication of thesis work.]

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Appendix A

**THERMODYNAMIC DERIVATIONS: A GAUSSIAN DENSITY
OF STATES IN PEL THEORY**

The included derivations correspond to Equations 1.10 - 1.14 in Chapter 1.2.

Starting with the equation for a Gaussian density of states to describe the inherent energy states available to a glass system, with Φ the potential energy of an inherent state,

$$D(\Phi) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(\Phi - \bar{\Phi})^2}{2\sigma^2}\right] = \frac{1 \text{ state}}{\text{atom}}, \quad (\text{A.1})$$

one can then define a general equation for the partition function:

$$\mathbf{Z} = \int D(\Phi) \exp\left[\frac{-\Phi}{kT}\right] d\Phi. \quad (\text{A.2})$$

Substituting in $D(\Phi)$ gives

$$\mathbf{Z} = \frac{1}{\sigma\sqrt{2\pi}} \int \exp\left[-\frac{(\Phi - \bar{\Phi})^2}{2\sigma^2}\right] \exp\left[\frac{-\Phi}{kT}\right] d\Phi, \quad (\text{A.3})$$

where $\bar{\Phi}$ goes to zero with Gaussian center set at zero.

Simplifying the exponential terms,

$$\mathbf{Z} = \frac{1}{\sigma\sqrt{2\pi}} \int \exp\left[-\left(\frac{\Phi^2}{2\sigma^2} + \frac{\Phi}{kT}\right)\right] d\Phi. \quad (\text{A.4})$$

Complete the square of bracketed exponential term in A.4 to define a new Gaussian as Φ' by first rearranging to

$$\Phi^2 + \frac{2\sigma^2}{kT}\Phi. \quad (\text{A.5})$$

One can then complete the square

$$\left[\left(\Phi + \frac{\sigma^2}{kT} \right)^2 - \left(\frac{\sigma^2}{kT} \right)^2 \right], \quad (\text{A.6})$$

and set

$$\Phi' = \left(\Phi + \frac{\sigma^2}{kT} \right) \quad (\text{A.7})$$

to substitute back into the exponential and distributing the negative sign.

$$Z = \frac{1}{\sigma\sqrt{2\pi}} \int \exp \left[- \left(\Phi + \frac{\sigma^2}{kT} \right)^2 + \left(\frac{\sigma^2}{kT} \right)^2 \right] d\Phi. \quad (\text{A.8})$$

$$Z = \frac{1}{\sigma\sqrt{2\pi}} \exp \left(\frac{\sigma^2}{kT} \right)^2 \int \exp(-\Phi')^2 d\Phi. \quad (\text{A.9})$$

The integral expression in A.9 becomes $\sqrt{\pi}$ due to the Gaussian integral relationship $\int_{-\infty}^{\infty} \exp -a(x + b)^2 dx = \sqrt{\frac{\pi}{a}}$ where $a > 0$.

Where the $\sqrt{\pi}$ cancels with the denominator to form the partition function with a Gaussian configurational density of states,

$$Z(\Phi, T) = \frac{1}{\sigma\sqrt{2}} \exp \left(\frac{\sigma^2}{kT} \right)^2. \quad (\text{A.10})$$

Utilizing this partition function, the thermodynamic state functions can be defined, i.e., Helmholtz free energy (F), entropy (S), internal energy (U), enthalpy (H), and heat capacity (C_p).

Starting with the Helmholtz free energy (F), the derivations are carried out below utilizing relationships defined in Morse.[32]

$$\begin{aligned} F &= -kT \ln(Z) \\ &= -kT \ln \left[\frac{1}{\sigma\sqrt{2}} \exp \left(\frac{\sigma^2}{kT} \right)^2 \right] \\ &= -kT \ln \left(\frac{1}{\sigma\sqrt{2}} \right) - kT \left(\frac{\sigma^2}{kT} \right)^2 \\ &= +kT \ln \sigma\sqrt{2} - \frac{\sigma^4}{kT} \end{aligned}$$

Then for Entropy,

$$\begin{aligned} S &= -\frac{dF}{dT} \\ &= -k \ln(\sigma\sqrt{2}) - \frac{\sigma^4}{kT^2} \end{aligned}$$

For internal energy,

$$\begin{aligned} U &= F + TS \\ &= kT \ln(\sigma\sqrt{2}) - \frac{\sigma^4}{kT} + \frac{-\sigma^4}{kT^2}T \\ &= \gamma - \frac{2\sigma^4}{kT}, \end{aligned}$$

where $\gamma = kT \ln(\sigma\sqrt{2})$.

Enthalpy (H) can be simplified with a simple observation: $dH = dU + VdP$, where VdP is negligible due to the constant ambient pressure in standard DSC experiments.

Thus,

$$H = U = \gamma - \frac{2\sigma^4}{kT}. \quad (\text{A.11})$$

Through the PEL and corresponding assumptions leading to a Gaussian distribution-based partition function outlined above, enthalpy has a T^{-1} dependence (correlated with the $n=1$ dependence in Chapter 2).

Finally, through the above assumptions, the Gaussian landscape constant pressure heat capacity (C_p) has a T^{-2} dependence;

$$C_p = \frac{dU}{dT} = \gamma + \frac{2\sigma^2}{kT^2}. \quad (\text{A.12})$$

Appendix B

SUPPLEMENTAL MATERIALS FOR CHAPTER 2

B.1 Underlying Assumptions

There are some fundamental assumptions made in this work that streamline the mathematics. Starting from first principles and the First Law of Thermodynamics, we derive our mathematical representation for configurational enthalpy and its underlying concepts. Through fundamental expansions and indexed steps, the enthalpy is described as a function of the potential energy with the kinetic energy scaling only with temperature.

From the First Law, $U = TS - PV$, its perfect differential $dU = TdS - PdV$, and the fundamental expression for enthalpy, $H = U + PV$, the enthalpic differential is determined as $dH = dU + VdP$.^[32] Under the conditions of this work $V = 10^{-5}m^3mol^{-1}$, and $P = 1 \text{ atm} = 10^5 \text{ Pa}$. Thus, $VdP = 1Jmol^{-1}$ and is negligible compared to the experimental h_{Config} of $10kJmol^{-1}$. This simplification yields enthalpy as a strict function of internal energy, U . Expanding this energy, however, reveals $U = PE + KE$ with the potential energy (PE) represented now as ϕ , and the kinetic energy is known as $\frac{3k_B T}{2}$ from the equipartition theorem (equipartition theorem of ideal gas states each degree of freedom of kinetic energy is $\frac{k_B T}{2}$. In three dimensions this yields $\frac{3k_B T}{2}$).^[32]

Probing deeper into the potential energy description, ϕ can be expanded; $\phi = \phi^l - \phi^x$, with ϕ^l and ϕ^x the potential energy of the liquid and crystalline components, respectively. Each can then be expanded further into configurational and vibrational terms:

$$\begin{aligned}\phi^l &= \phi_{Config}^l + \phi_{vib}^l = \phi_{Config}^l + \phi_{vib,har}^l + \phi_{vib,anh}^l \\ \phi^x &= \phi_{Config}^x + \phi_{vib}^x = \phi_{Config}^x + \phi_{vib,har}^x + \phi_{vib,anh}^x\end{aligned}$$

where the vibrational term contains separable harmonic and anharmonic components.

Substituting terms,

$$\begin{aligned}\phi &= \phi^l - \phi^x \\ &= \phi_{Config}^l - \phi_{Config}^x + \phi_{vib,har}^l - \phi_{vib,har}^x + \phi_{vib,anh}^l - \phi_{vib,anh}^x\end{aligned}$$

can be simplified via two approximations. The harmonic approximation utilizes the Dulong-Petit heat capacity of $3R$ as a description of the harmonic component of the potential energy. With $C_{P,har} = 3R = \phi^l + \phi^x$, the two terms split evenly yielding $\phi^l = \phi^x = \frac{3R}{2}$. The anharmonic approximation emphasizes the Debye-Grüneisen anharmonic heat capacity, $C_P - C_V = \alpha^2 B \nu T$ with α the coefficient of thermal expansion, B the isothermal bulk modulus, ν the molar volume, and T the temperature in Kelvin. When calculated, the $\phi_{vib,anh}^l$ and $\phi_{vib,anh}^x$ values are negligible compared to the Dulong-Petit ($25 Jmol^{-1}$) and experimental enthalpy measurements ($10 kJmol^{-1}$). These components are thus neglected.

The equations for potential energy and enthalpy simplify to a configurational dependence, $\phi = \phi^l - \phi^x = \phi_{Config}^l - \phi_{Config}^x = \phi_{Config}^{lx}$, and $H = U = \frac{3k_B T}{2} + \phi$ with a standardized kinetic energy term. From this, the enthalpy is termed the configurational energy in this work:

$$H = H_C = \phi_{Config}^{lx} + \frac{3k_B T}{2},$$

where H can be offset by the kinetic energy term, $H - \frac{3k_B T}{2} = \phi_{Config}^{lx}$, thus the configurational enthalpy is truly a measure of the change in potential energy between the liquid and crystal through various phase transformations (glass transition, crystallization, and melt).

Given configurational enthalpy is reported in units of J/g, the various thermodynamic variables discussed here are all specific values. Thus, $H_C = h_C$; $S_C = s_C$; $C_V = c_V$. Further, while here configurational components are denoted by the subscript "Config" for clarify, the text utilizes the subscript "c" for concision.

B.2 Entropy Derivation: Equivalence of Equation 2.1 and 2.2

In the text, Equation 2.2 is derived from 2.1. Below is an outline of the steps. Starting with Equation 2.1,

$$h_C(T) = h_C(\infty) \left[1 - \left(\frac{\theta_h}{T} \right)^n \right]$$

the specific heat capacity becomes

$$\begin{aligned}
 c_V &= \frac{\partial Q(T)}{\partial T} = \frac{\partial U(T)}{\partial T} = \frac{\partial h_C(T)}{\partial T} = \frac{\partial}{\partial T} \left(h_C(\infty) - \frac{h_C(\infty)\theta_h^n}{T^n} \right) \\
 &= \frac{\partial}{\partial T} (h_C(T))_{T=\infty} - \frac{\partial}{\partial T} \left(\frac{h_C(\infty)\theta_h^n}{T^n} \right) \\
 &= c_{V,\infty} - \left(\frac{\theta_h^n}{T^n} c_V(T) \right)_{T=\infty} + \frac{nh_C(\infty)\theta_h^n}{T^n} \\
 &= c_{V,\infty} + \frac{nh_C(\infty)\theta_h^n}{T^{n+1}}.
 \end{aligned}$$

When ignoring the pressure dependence of $h_C(\infty)$ and θ_h at ambient pressure; i.e., ignoring the PV term in the free energy, c_C is obtained:

$$c_C = \frac{nh_C(\infty)\theta_h^n}{T^{n+1}}$$

For the entropy, toward the high-temperature limit,

$$\begin{aligned}
 s_C &= \int_T^\infty \frac{c_V}{T} dT = \int_T^\infty \left(\frac{c_{V,\infty}}{T} + \frac{nh_C(\infty)\theta_h^n}{T^{n+2}} \right) \\
 &= s_{C,\infty} + \frac{nh_C(\infty)\theta_h^n}{n+1} \frac{1}{T^{n+1}}
 \end{aligned}$$

Now change the above expression for configurational entropy to the familiar micro-canonical form. Multiply the second term of the configurational enthalpy by

$$s_C = s_{C,\infty} + \frac{nh_c(\infty)}{\theta_h(n+1)} \left(\frac{\theta_h}{T} \right)^{n+1}$$

From equation "1",

$$\frac{h_C(\infty) - h_C(T)}{h_C(\infty)} = \left(\frac{\theta_h}{T} \right)^n$$

or

$$\left(\frac{h_C(\infty) - h_C(T)}{h_C(\infty)} \right)^{\frac{1}{n}} = \left(\frac{\theta_h}{T} \right)$$

So

$$\left(\frac{\theta_h}{T} \right)^{n+1} = \left(\frac{h_C(\infty) - h_C(T)}{h_C(\infty)} \right)^{\frac{1}{n}} \left(\frac{h_C(\infty) - h_C(T)}{h_C(\infty)} \right) = \left(\frac{h_C(\infty) - h_C(T)}{h_C(\infty)} \right)^{\frac{n+1}{n}}$$

where

$$s_C = s_{C,\infty} - \frac{nh_c(\infty)}{\theta_h(n+1)} \left(\frac{h_C(\infty) - h_C(T)}{h_C(\infty)} \right)^{\frac{n+1}{n}} = s_{C,\infty} - C \left(\frac{h_C(\infty) - h_C(T)}{h_C(\infty)} \right)^{\frac{n+1}{n}}$$

With Equation 2.2 in Chapter 2 written in terms of configurational potential energies ϕ and ϕ_0 , these are equivalent to h_C and h_∞ , respectively, given the prior assumptions, with C a constant. The above equation generalizes to Equation 2.2. So the above exhibits the derivation from Equation 2.1 to 2.2,

$$s_c(\phi) \propto s_C(\phi_0) - C(\phi_0 - \phi)^{\frac{n+1}{n}}$$

B.3 Sn Heating Rate Temperature Correction

DTA runs were completed on pure Sn (99.999%) at incremental heating rates from 0.5 to 20 K/min. These heat flow curves are plotted in Figure B.1 and increased peak broadening and peak shift are observed at higher heating rates. This peak broadening and shift effect are the results of thermal lag in the system, where the sample has not yet caught up to the temperature at the thermocouple. These peak shift corrections (Table B.1) are utilized in calculating accurate enthalpy peak temperatures as discussed in Section 2.4.

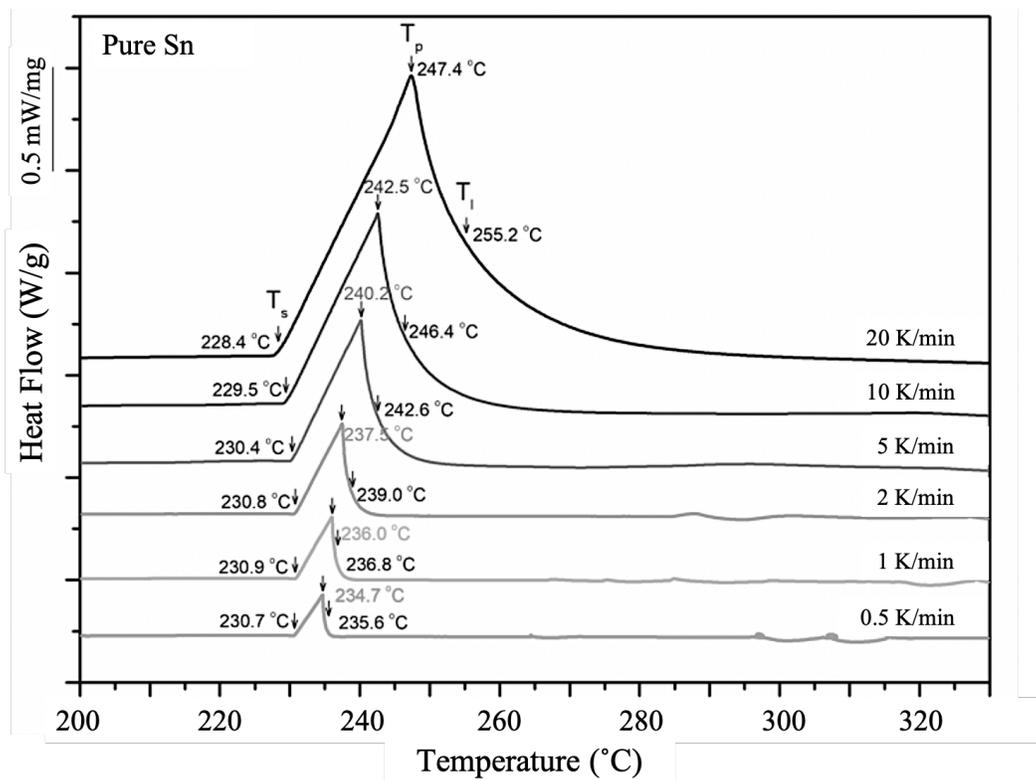


Figure B.1: Sn heat flow responses with respect to heating rate.

The correction values utilized are as follows:

Heating Rate (K/min)	Temperature Correction (K)
0.1	0
0.2	0
0.5	0
1	-0.8
1.5	-1
2	-1.5
3	-2
5	-4.2
8	-5.2
10	-6.5
15	-9
20	-11

Table B.1: Peak offset correction values from Figure B.1.

	Cu_{14}	Cu_{16}	Cu_{18}	Cu_{20}	Cu_{23}	Cu_{27}
T_{gm} (K)	533	548	551	-	-	651
Δh_C (J/g)	27	20	23.7	-	-	15.7

Table B.2: Raw data accompanying Figure 2.11 identifying the trend of fragility, copper content, glass-melting temperature, and latent heat of glass-melting.

B.4 Raw Data

Raw data are included in the supplemental material excel file included in the CaltechThesis archive.

Appendix C

SUPPLEMENTAL MATERIALS FOR CHAPTER 3

C.1 Raw Data

Raw data are included in the supplemental material excel file included in the CaltechThesis archive.

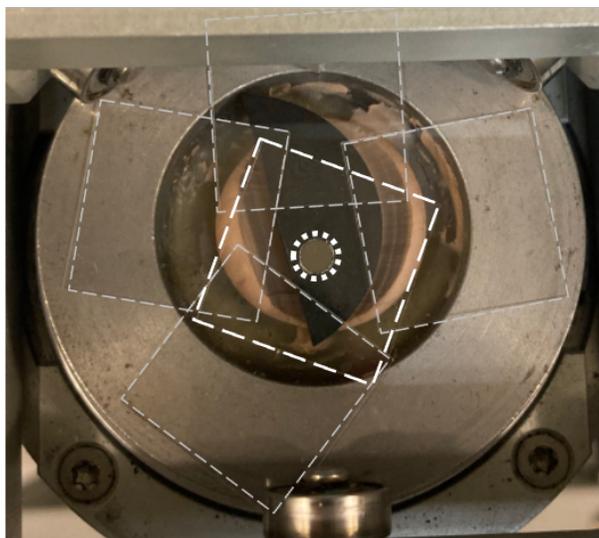


Figure C.1: Cover slip location for carbon-puck masking method. Central cover slip with hole highlighted with white borders on free edges. Full cover slips outlined by grey dashed lines.

Appendix D

SUPPLEMENTAL MATERIALS FOR CHAPTER 4

Compiled supporting materials for Chapter 4.

[These supplemental materials are embargoed pending publication.]

*Appendix E***RESOURCES FOR SURVIVING GRADUATE SCHOOL****E.1 The "Snake Fight" Portion of Your Thesis Defense by Luke Burns**

FAQ:

Q: Do I have to kill the snake?

A: University guidelines state that you have to “defeat” the snake. There are many ways to accomplish this. Lots of students choose to wrestle the snake. Some construct decoys and elaborate traps to confuse and then ensnare the snake. One student brought a flute and played a song to lull the snake to sleep. Then he threw the snake out a window.

Q: Does everyone fight the same snake?

A: No. You will fight one of the many snakes that are kept on campus by the facilities department.

Q: Are the snakes big?

A: We have lots of different snakes. The quality of your work determines which snake you will fight. The better your thesis is, the smaller the snake will be.

Q: Does my thesis adviser pick the snake?

A: No. Your adviser just tells the guy who picks the snakes how good your thesis was.

Q: What does it mean if I get a small snake that is also very strong?

A: Snake-picking is not an exact science. The size of the snake is the main factor. The snake may be very strong, or it may be very weak. It may be of Asian, African, or South American origin. It may constrict its victims and then swallow them whole, or it may use venom to blind and/or paralyze its prey. You shouldn't read too much into these other characteristics. Although if you get a poisonous snake, it often means that there was a problem with the formatting of your bibliography.

Q: When and where do I fight the snake? Does the school have some kind of pit or arena for snake fights?

A: You fight the snake in the room you have reserved for your defense. The fight generally starts after you have finished answering questions about your thesis. However, the snake will be lurking in the room the whole time and it can strike at any point. If the snake attacks prematurely it's obviously better to defeat it and get back to the rest of your defense as quickly as possible.

Q: Would someone who wrote a bad thesis and defeated a large snake get the same grade as someone who wrote a good thesis and defeated a small snake?

A: Yes.

Q: So then couldn't you just fight a snake in lieu of actually writing a thesis?

A: Technically, yes. But in that case the snake would be very big. Very big, indeed.

Q: Could the snake kill me?

A: That almost never happens. But if you're worried, just make sure that you write a good thesis.

Q: Why do I have to do this?

A: Snake fighting is one of the great traditions of higher education. It may seem somewhat antiquated and silly, like the robes we wear at graduation, but fighting a snake is an important part of the history and culture of every reputable university. Almost everyone with an advanced degree has gone through this process. Notable figures such as John Foster Dulles, Philip Roth, and Doris Kearns Goodwin (to name but a few) have all had to defeat at least one snake in single combat.

Q: This whole snake thing is just a metaphor, right?

A: I assure you, the snakes are very real.