Thermophysical and Structural Measurements of Liquid Metallic Alloys Using Electrostatic Levitation

James Christopher Bendert
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Thermophysical and Structural Measurements of Liquid Metallic Alloys Using Electrostatic Levitation

by

James Christopher Bendert

A dissertation presented to the
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of Doctor of Philosophy

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James Christopher Bendert

Washington University in Saint Louis

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ABSTRACT OF THE DISSERTATION

Thermophysical and Structural Measurements of Liquid Metallic Alloys Using Electrostatic Levitation

by

James Christopher Bendert

Doctor of Philosophy in Physics

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Professor Kenneth F. Kelton, Chairperson

In the study of the glass transition, the properties of high temperature liquids in their equilibrium and supercooled states may provide clues to the question of why certain compositions form glasses more easily than others. In metallic alloys such measurements are difficult due to the high reactivity and high melting temperatures of these liquids. Levitation methods provide a solution this problem by isolating liquid alloys from their environments. Here, the techniques of data acquisition and analysis for thermophysical property measurements under electrostatic levitation are presented, with demonstrative examples from select compositions from the Cu-Zr system. The development of techniques and software for the analysis of X-ray diffraction data acquired using electrostatic levitation is also discussed and applied to amorphous Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$. The results of systematic studies of density and viscosity as a function of temperature in Cu$_{100-x}$Zr$_x$ ($x = 30 - 55$) reveal maxima in thermal expansion coefficient and kinetic strength at the best compositions of the alloy system. Interpretation of these results predicted a temperature dependence of the thermal expansion
coefficient on supercooling. This prediction was confirmed by high precision measurements of density in Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ and Zr$_{57}$Cu$_{15.4}$Ni$_{12.6}$Al$_{10}$Nb$_{5}$ on cooling through the glass transition during electrostatic levitation.
Preface

This dissertation presents work conducted from June 2009 through April 2013 in the laboratory of Professor Kenneth F. Kelton in the Department of Physics at Washington University in St. Louis. During this time the author led the development of data acquisition, reduction and analysis for thermophysical (Ch. 2) and X-ray diffraction (Ch. 3) measurements in the Washington University beamline electrostatic levitator (WU-BESL). A collection of LabVIEW™ programs created to perform these functions can be found on the included DVD. The application of these techniques to the Cu$_{100-x}$Zr$_x$, Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ and Zr$_{57}$Cu$_{15.4}$Ni$_{12.6}$Al$_{10}$Nb$_5$ systems furthered the developments of these methods, as well as provided insights into the relationships between thermophysical properties of the high temperature liquid and the glass forming ability (Ch. 4). All sections from these chapters have been submitted for publication in peer reviewed journals at the time of this writing. Portions of submitted manuscripts have been excerpted and/or modified for use in this dissertation.
Chapter 1

Introduction

In high temperature liquids, atomic associations and order rapidly form and dissolve. As the liquids cool, preferred low-energy structures develop. Cooling further, kinetics slow and local clusters linger in their low-energy configurations. Local structural ordering, requiring the rearrangement of only a few atoms, is still rapidly developed and destroyed, but long-range ordering is prevented by the energy barriers to large atomic rearrangements. Upon cooling even further, all structural change become difficult and eventually the system becomes locked, forming a glass.

Though this description of glass formation is beautiful in its simplicity, the details of glass formation for metallic alloys are still unclear. Why some compositions form glasses more easily than others is only understood in the broadest terms, but may be manifest in the bulk properties of the glass forming liquid. This dissertation investigates these properties of high temperature metallic liquids, with the purpose of improving the understanding of the relationships of bulk properties and glass forming ability. This chapter will begin with a general overview of glasses and the glass transition (Sect. 1.1). This will motivate the discussion of glass forming ability (Sect. 1.2) and the use of electrostatic levitation (ESL)
for the of study metallic liquids (Sect. 1.3). In Ch. 2 and 3, methods for measuring structural and thermophysical properties of high temperature liquids using electrostatic levitation are described. In Ch. 4, the thermophysical measurement techniques are applied, identifying correlations with glass forming ability between density, thermal expansion coefficient, viscosity and kinetic fragility.

1.1 Glasses and the Glass Transition

Although the term glass is synonymous with soda-lime-silicate glass (72% SiO$_2$+14.2% Na$_2$O+2.5% MgO+10% CaO+ 0.6% Al$_2$O$_3$), any liquid cooled rapidly enough to avert crystallization vitrifies (i.e., forms a glass). Contrary to the popular belief that glasses flow, they have a definite shape and volume. A glass is defined as an amorphous solid, meaning that unlike crystals, the atoms in the materials cannot be found in a repeating pattern, as is illustrated in Fig. 1.1. This should not be confused with randomness. In the two-dimensional example in Fig. 1.1.b, the number of the bonds and the bond angles are constrained, which results in significant short and medium range order.

A glass forms when a liquid is cooled below its glass transition temperature, $T_g$, without crystallization. $T_g$ is the temperature at which the dynamics of the liquid slow to the point that atoms become ‘locked’ in their positions (defined in terms of viscosity as $10^{12}$ Pa-s). This distinguishes a glass from a liquid, because in liquids atoms are mobile and able to sample every available configuration (i.e., liquids are ergodic). At the glass transition, ergodicity is broken and the behavior of the material abruptly changes character. On cooling through the glass transition, the first derivatives of the Gibb’s free energy (e.g., specific volume and entropy) abruptly change slope (Fig. 1.2.a). Second derivatives (e.g., thermal expansion
coefficient and specific heat) undergo an abrupt, but not quite discontinuous, drop at $T_g$. This drop has the appearance of a ‘diffuse second order phase transition’ (Fig. 1.2.b) [1].
Ergodicity can be understood through the concept of an energy-landscape. This is a statistical mechanical construct in which each possible configuration of the atoms in a material is a point on a 3N+1 dimensional landscape. The peaks and valleys of this landscape correspond to high and low energy configurations, respectively [2]. Movement across this landscape is achieved by atomic rearrangement, where ‘local’ movement requires only minor rearrangements of the atoms. The profile across one of the dimensions of the landscape might appear as shown in Fig. 1.3.

![Energy Landscape Diagram](image)

Figure 1.3: Schematic illustration of an energy landscape. The x-axis represents all configurational coordinates. [Reprinted by permission from Macmillan Publishers Ltd: NATURE [3], copyright (2001)]

The probability of sampling a configuration of energy $E$ is determined by Boltzmann statistics,

$$P(E) = \exp \left( \frac{-E}{k_B T} \right) / \sum_i \exp \left( \frac{-E_i}{k_B T} \right),$$  \hspace{1cm} \text{(1.1)}$$

where $k_B$ is the Boltzmann’s constant and $T$ is temperature. Although the crystal state is the lowest energy configuration (and therefore has the highest probability), it is only a small fraction of the possible configurations. There are, however, a large number of relatively low
energy configurations, any of which the liquid might occupy with nearly equal probability as the crystal states. This group of low energy configurations is called the ideal glass basin, because when a liquid cools slowly into a glass there is a high probability it will occupy one of these states. In these configurations the glass is metastable, which means that it is a local energy minimum, but not the global minimum (the crystal).

There may be multiple glass basins on the energy landscape that the ergodic liquid samples. The process of transitioning from one energy basin to another is called α-relaxation, while state transitions within a basin are achieved by β-relaxation. At high temperatures, where the liquid can freely diffuse over the energy landscape, α and β-relaxation times are equal. On cooling the liquid, the relative heights of the energy barriers between basins become more significant, slowing α-relaxation. The temperature at which α and β-relaxation begin to diverge is called the crossover temperature (sometimes associated with mode-coupling theories). On cooling further, the glass transition is marked by disappearance of α-relaxation, preventing the transition between basins and breaking ergodicity. Whether a liquid is frozen into a higher energy over the lower energy basin depends on the rate the liquid is cooled.

If a liquid has a large number of basins on its energy landscape, α-relaxation processes will dominate atomic diffusion. This would be manifest in the measured viscosity, η, of the liquid as a sharp rise in η preceding the glass transition, as barriers to α-relaxation increase. If a liquid has only one, or a few, large basins on the energy landscape, β-relaxation will dominate so that viscosity will follow the temperature dependence of an activated process. Activated processes follow an Arrhenius temperature dependence,

\[ \eta = \eta_0 \exp \left( \frac{E_A}{T} \right) \]  

(1.2)
where $E_A$ is the activation energy of the process and $\eta_0$ is a constant. In the liquid classification scheme introduced by Angell, the former liquid would be defined as fragile while the latter liquid would be classified as strong (Fig. 1.4) [4]. To distinguish Angell’s strong and fragile classification from the mechanical properties, liquids with these characteristics are referred to as kinetically strong or fragile.

Figure 1.4: Angell plot of viscosity $\eta$ versus inverse temperature (normalized to the glass transition) $T_g/T$ for fragile and strong liquids with schematic representations of their corresponding energy landscapes.
1.2 Glass Forming Ability

Glassy materials are remarkably prevalent in everyday experience. Glasses can be found in food (gelatin), plumbing (PVC, polyvinyl chloride), cookware (Pyrex, 81% SiO$_2$ + 12% B$_2$O$_3$ + 4.5% Na$_2$O + 2.0% Al$_2$O$_3$), fiber optics (90% Al$_2$O$_3$ + 10% GeO$_2$), computer memory (OUMs, Ge$_2$Sb$_2$Te$_5$), pharmaceuticals (Indomethacin), and elsewhere. Network glasses and polymers, however, dominate everyday exposure to amorphous materials. This is due to the ease by which they form glasses, also known as their glass forming ability (GFA).

GFA is measured by the critical cooling rate, which is the slowest cooling rate the liquid can be cooled into a glass without crystallization. A slower critical cooling rate indicates a better glass former. In metallic systems, the critical casting thickness (i.e., the largest thickness a glass can be cast) is often used as a measure of GFA. A higher critical casting thickness is achievable with a slower critical cooling rate and therefore indicates a better glass former.

The key to high GFA is the avoidance of crystallization. Crystallization from the supercooled liquid (i.e., cooled below the equilibrium melting temperature) requires atomic or molecular rearrangement in the liquid in order to form clusters of atoms belonging to the new phase. This process is called nucleation, which is homogeneous or heterogeneous depending on whether the process is spontaneous or catalyzed. In classical nucleation theory, the work required to form a cluster of $n$ molecules in a new phase is,

$$W(n) = n\Delta\mu + \sigma A,$$

(1.3)

where $\Delta\mu$ is the difference in the free energy per molecule between phases, $\sigma$ is the interfacial free energy between the new and old phase, and $A$ is the surface area of the cluster. Only
when nuclei (i.e., clusters of the new phase) become larger than the critical size (where \( \frac{dW(n)}{dn} = 0 \)) is it energetically favorable to grow. In the Volmer-Weber kinetic model of nucleation, the growth of nuclei is a kinetic process requiring atoms to ‘attach’ to the nucleating phase in order to move to higher cluster size \([5]\). This identifies three factors which promote or inhibit crystallization: (i) the difference in Gibb’s free energy between the initial and final phase, (ii) the structural differences between the two phases (as encompassed by the concept of interfacial energy), and (iii) atomic kinetics. It is within this context that GFA is interpreted.

In metallic systems, which are the focus of this dissertation, empirical rules have been established identifying glass forming compositions in multicomponent systems: (i) the multicomponent system should consist of three or more elements, (ii) there should be a significant difference (greater than \( \approx 12\% \)) in the atomic sizes of the main constituent elements, and (iii) the elements should have negative heats of mixing. These rules are empirical, but can be understood as promoting multicomponent short-range interactions, as diagrammed in Fig. 1.5 \([6]\). These interactions would be in conflict with crystalline order, so that nucleation is inhibited by an increase in the interfacial energy between phases, and crystal growth is inhibited by the need for significant atomic rearrangements. In addition, the multicomponent interactions increase the difficulty of atomic rearrangements, inhibiting kinetics.

Within a given alloy system, another empirical rule is that bulk metallic glass formers (BMGs, which are metallic glass formers with critical casting thickness greater than 1 mm) are found at, or near, eutectic compositions. The first metallic glass reported, \( \text{Au}_{75}\text{Si}_{25} \) \([7]\), was found near the eutectic composition of the Au-Si phase diagram (Fig. 1.6). At this composition, the liquid remains in equilibrium several hundred degrees below the melting temperature of either pure element. This promotes glass formation in several ways. It reduces the
supercooled region, decreasing the driving free energy for crystal formation and the time spent out of equilibrium when cooling. Lowering the liquidus temperature also decreases the kinetics in the temperature region where nucleation and growth would occur.

There are exceptions to this rule, however. In the Cu-Zr binary system there are three BMG forming compositions: Cu$_{50}$Zr$_{50}$, Cu$_{64}$Zr$_{36}$ and Cu$_{54}$Zr$_{46}$ [9]. As shown in Fig. 1.7, two of these three compositions are eutectics; Cu$_{50}$Zr$_{50}$ is not. Additionally, Cu$_{64}$Zr$_{36}$ has the highest critical casting thickness despite having the highest liquidus of the three compositions. In Ch. 4, it will be shown that these compositions have the highest GFA because they are the least kinetically fragile liquids in the alloy system.
Figure 1.6: Au-Si eutectic phase diagram. (Reprinted from [8] with kind permission from Springer Science and Business Media)
Figure 1.7: Cu-Zr phase diagram. (Reprinted from [10] with kind permission from Springer Science and Business Media)
1.3 Electrostatic Levitation (ESL)

There are two approaches to studying glasses and the glass transition: ‘from the glass’ or ‘from the liquid’, referring to whether the study is conducted on heating from an amorphous state or cooling from the liquid. The ‘from the glass’ approach often suffers from inconsistency due to the kinetic nature of the glass transition. As previously noted, the state of the glass depends on cooling rate and therefore production methodology. Although the supercooled liquid may be studied by heating from the glass, in many systems only a small temperature range in the vicinity of the glass transition may be accessible before crystallization. Traditionally, in metallic liquids, the ‘from the liquid’ approach is even worse. Metallic alloys have high melting temperatures, and are highly reactive in the liquid state. Furthermore, heterogeneous nucleation from container surfaces prevents supercooling in metallic alloys.

The measurement of the properties of liquid metallic alloys in the equilibrium and supercooled states can be achieved by isolating the metals from their environments. For this purpose levitation techniques have been developed, including electromagnetic levitation (EML) and electrostatic levitation (ESL). In EML, samples are levitated by coupling eddy currents induced in the material to an applied RF field. In ESL, samples are capacitively charged and levitated in a dynamically maintained electric field. Although EML has advantages (particularly when performed in micro gravity [11]), heat is coupled to levitation which decreases the cooling rates achievable during a measurement. In ESL, samples are smaller and laser-heated, which allows for the study of both high and low melting temperature alloys in their equilibrium liquid and supercooled states. To this end, an electrostatic levitation facility designed for integration with the MUCAT synchrotron beamline at Argonne National
Laboratory was constructed at Washington University (WU-BESL, Fig. 1.8.a) by Nicholas Mauro [12,13].

Figure 1.8: (a) The Washington University beamline electrostatic levitation facility and (b) diagram of optical sources and detectors as of 06/2012.

The WU-BESL floats 10-150 mg (2-4 mm diameter) samples in high vacuum ($\sim 10^{-7}$ Torr) in an electric field of 0 to 2.5 MV/m. Measurements in the WU-BESL include temperature, volume, position, shape, and X-ray diffraction. During these measurements, samples are heated by infrared laser and charge is maintained during processing using ultraviolet sources. A schematic illustration of the optical sources and detectors for measurements and control in the WU-BESL is shown in Fig. 1.8.b.
Levitation is achieved by maintaining the electrostatic forces to counter gravity between vertically \((z)\) aligned electrodes. Orthogonal side electrodes apply \(\pm 3\) kV to maintain horizontal \((x - y)\) position to within \(\pm 45\mu m\) (Fig. 1.9.a). The curvature of the top electrode promotes stability in the \(x - y\) plane. The solution to the axially symmetric Laplace equation,

\[
\nabla^2 V = \frac{\partial^2 V}{\partial r^2} + \frac{1}{r} \frac{\partial V}{\partial r} + \frac{\partial^2 V}{\partial z^2},
\]

for a curved top electrode reveals that the central axis is a minimum in the electric potential along the radius coordinate \(r\) (Fig. 1.9.b). This minimum deepens with steepness of the curvature, improving sample localization in the \(x - y\) plane. The curvature in the electrode increases the non-linearity along the \(z\)-axis which, when gravitational potential is subtracted, creates a potential maximum. A 15 mm radius of curvature was selected to balance these two-competing effects.

Figure 1.9: (a) The WU-BESL electrode assembly, with levitated sample, and (b) a simulation of the potential energy field (combined gravitational and electrical) for a point sample floating in an ESL.
Since the sample must be maintained at a three-dimensional saddle point, voltages are dynamically controlled to maintain position. To do this, the sample location is detected by shadows cast on orthogonal position sensitive detectors (PSDs). Positioning information is input into a computer, which adjusts to the voltages to damp the sample momentum and maintain position [14].

The optics and light sources for shadow detection have gone through several iterations since the WU-BESL’s original construction, including red laser diodes, Helium-Neon lasers and, as of June 2012, colored LEDs with focusing optics. The LED optical configuration for position detection is shown in Fig. 1.10. Along the \( y \)-axis this design was modified to incorporate viscosity measurements (see Sect. 2.2). The use of LEDs with these optics results an inverted image with a magnification of \( \approx 1.5 \) times. The increased magnification, over laser sources, was found to increase the detector sensitivity and decrease the sensitivity of the sample positioning to the alignment of the PSD with its backlight.

![Figure 1.10: Schematic of LED positioning optics along the \( y \)-axis (not to scale).](image)

Further details of the thermophysical measurements will be discussed in Ch. 2. Details of the construction of WU-BESL, beamline incorporation and data acquisition can be found elsewhere [13].
1.4 References


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Chapter 2

Thermophysical Property Measurements in Electrostatic Levitation

The original purpose of the modern ESL was to study nucleation kinetics, the creation of metastable phases and thermophysical properties of supercooled liquids for a broad range of materials in a non-reactive containerless environment [1]. To satisfy this purpose, a series of non-contact measurements have been developed, or adapted from other containerless systems. The non-contact constraint makes any measurement a challenge, as it fundamentally limits measurements to those that utilize optical sensors or electromagnetic field manipulation. The most common measurements in ESL are temperature, density, surface tension and viscosity. In this chapter, WU-BESL’s temperature (Sect. 2.1), density and viscosity (Sect. 2.2) measurements are described with examples from select Cu-Zr compositions. Specific heat can also be acquired using electrostatic levitation through the analysis of the temperature data; this is described with an application in Sect. 4.3. Sections 2.1 and 2.2
were submitted as individual manuscripts to the proceedings of the 18th Symposium on Thermophysical Properties to be published in the *International Journal of Thermophysics*.

Although volume integration for density measurements is described briefly in Sect. 2.2, step-by-step descriptions of the integration algorithms used the accompanying software are found in Appendix A. A user’s guide for WU-BESL density acquisition and analysis is found in Appendix B.

2.1 Temperature Calibration for Optical Pyrometry in Containerless Systems using Differential Scanning Calorimetry — Application to Cu\(_{100-x}\)Zr\(_x\) (\(x = 45 - 50\)) [2]

2.1.1 Introduction

The most fundamental measurement for thermophysical property analysis is that of temperature. In most cases temperature is the independent thermodynamic variable over which all other measurements are taken. Accurate and precise measurements of the temperature are also important for controlling many experimental conditions. In containerless processing systems, such as electrostatic levitation (ESL) and electromagnetic levitation (EML), temperature measurements are made using optical pyrometers typically operating in the infrared range.
Infrared pyrometers operate by measuring the power emitted from an object within a frequency window integrated over the area observed, using the theory of blackbody radiation to calculate the temperature of the object. The spectral power per unit area, is given by
\[ P_{BB}(T, \lambda) = \frac{2\pi hc^2}{\lambda^5 \left(e^{\frac{hc}{k_B T}} - 1\right)}, \] (2.1)

where \( h \) is Plank’s constant, \( c \) is the speed of light, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature and \( \lambda \) is the wavelength at which the power is measured. For short wavelengths Wien’s approximation is valid and the radiated power is an exponential function of temperature, described by
\[ P(T, \lambda) \sim \frac{2\pi hc^2}{\lambda^5} e^{-\frac{hc}{k_B T}} \text{ as } \frac{hc}{k_B T} \rightarrow \infty. \] (2.2)

A single-color infrared pyrometer, operating over a narrow spectral band, uses a rearrangement of Eq. 2.2 with a multiplicative correction factor to calculate the temperature.

Spectral power measurements suffer from experimental inefficiencies (e.g. imperfect alignment or absorbing windows) and deviations from the blackbody spectrum due to sample specific parameters such as thickness, shape, surface conditions and reflectivity. The latter is expressed in terms of the spectral emissivity, which is generally temperature and wavelength dependent. An additional multiplicative factor, due to the experimental efficiency, takes into account artificial reduction of the measured power that is independent of the sample. Since neither the spectral emissivity nor the experimental efficiency are generally known they are combined into an effective emissivity. The effective spectral emissivity \( \epsilon \) (referred to only as the emissivity for the remainder of this section) must be determined by calibration.
The uncertainty in this calibration must be considered for comparisons between different systems.

The typical method of emissivity calibration is to match a measured temperature to that of a known heat signature. In principal, this should be a direct method of calibration. In practice, however, the presence of multiple heat signatures, differences in emissivity in different phases, and the lack of available or accurate phase diagrams make this difficult. In this section, a method is described for temperature calibration for optical pyrometers used in an ESL. A differential scanning calorimeter (DSC) is used to measure the temperatures of phase transitions that have a heat signature in ESL. Measurements of Cu_{100-x}Zr_x (x = 45, 48, 49, 50) are made to demonstrate the method.

2.1.2  Experimental Apparatus and Procedures

2.1.2.1  Specimens and Their Purities

Samples of composition Cu_{50}Zr_{50}, Cu_{51}Zr_{49}, Cu_{52}Zr_{48} and Cu_{55}Zr_{45} were prepared using high-purity Cu (99.995%) and Zr (99.9+% with nominal 3% Hf and 580 ppm O) from one gram master ingots made by arc-melting in a high-purity Ar gas atmosphere (99.998%) on a water-cooled Cu hearth. The arc-melting chamber was evacuated to less than 100 mTorr and backfilled with Ar gas repeatedly (at least three times). A one gram Ti-Zr ingot was kept molten for about one minute to further reduce residual oxygen. Master ingots were melted three times to ensure a homogeneous composition. Ingots were discarded in case the mass loss exceeded 0.05%. The ESL (60-90 mg) and DSC samples (≈30 mg) were taken from pieces of the broken master ingots. ESL samples were reformed to an approximately spherical
shape by arc-melting. If the mass loss after preparation exceeded 0.5%, corresponding to a shift in composition of 0.25%, the samples were discarded.

2.1.2.2 Electrostatic Levitation

Apparatus

ESL is used for containerless studies of the high temperature liquids. This study was made using the recently constructed Washington University Beamline ESL, or WU-BESL [4], in which inductively charged samples 2.0 - 4.0 mm in diameter are levitated under high vacuum ($\sim 10^{-7}$ Torr) in an electrostatic field (0 to 2 MV/m). Orthogonal electrodes and a control algorithm maintain the sample position during processing, while an external UV source maintains charge. The sample heat balance, and therefore the temperature, is controlled with a 980 nm, 0 - 50 W, nlight Pearl\textsuperscript{TM} Model P4-050-0980-AIM diode laser.

2.1.2.3 Measurement Temperature

Optical Pyrometry

Two infrared pyrometers with overlapping ranges were used to measure temperature across the range of 160 to 2300 °C. At high temperatures ($\geq 700$ °C), measurements were acquired with a two-color Process Sensors Metis MQ22, which operates at 1.40 and 1.64 µm over a temperature range of 600 to 2300 °C. At low temperatures ($< 700$ °C) a Process Sensors Metis MI18 MB8 with a range of 160 to 800 °C and a central wavelength of 1.89 µm was utilized. The data were collected at a fixed emissivity and saved for later calibration in the format that is output from the pyrometer. For the ratio pyrometer three temperature
measurements were recorded, one each from the two wavelengths and one based on the ratio of two measurements.

In the ratio and single color (wavelength) pyrometers, the approximate form of the look-up table for the signal is a scaled version of Wien’s law (scaled to 1000 at the high end of the temperature range of the pyrometer). It can be described by

$$S = 1000e^{C\left(\frac{1}{T_{\text{High}}} - \frac{1}{T}\right)}, \quad (2.3)$$

where the curvature of the profile is determined by the scaling factor $C$. From Wien’s law a single-color pyrometer would have a scaling factor of $C_{\text{Color}} = \frac{hc}{k_B \lambda}$ (7618 K at 1.89 $\mu$m, 8779 K at 1.64 $\mu$m and 10284 K at 1.4 $\mu$m) and for ratio measurements $C_{\text{Ratio}} = \frac{hc(\lambda_1 - \lambda_2)}{k_B \lambda_2 \lambda_1}$ (1505 K for $\lambda_1 = 1.64$ $\mu$m and $\lambda_2 = 1.4$ $\mu$m).

An expression, based on Eq. 2.3, for an emissivity-corrected temperature (subscript 2) from a temperature recorded at a previous emissivity (subscript 1) is

$$T_2 = T_1 \frac{T_1}{1 - \frac{T_1}{C} \ln \left(\frac{\epsilon_1}{\epsilon_2}\right)}, \quad (2.4)$$

where for a ratio measurement $\epsilon_1$ and $\epsilon_2$ refer to the old and new emissivity ratios, rather than the emissivities. The temperature calibration is performed by adjusting the new emissivity so that an observed thermal signature in the temperature-time profile measured in ESL matches the temperature of a known phase transition.
Differential Scanning Calorimetry

In DSC, a sample and a reference pan are heated at a set rate while maintaining the two pans at the same temperature. The difference in power required to do this is measured as a function of temperature. Endothermic or exothermic transitions in the sample appear as peaks or dips in the power, marking potential calibration points for an optical pyrometer. Measurements of the solidus and liquidus temperatures were determined by the intersection of extrapolated baselines [5], with uncertainties estimated from the measurement variability.

A Setaram Instrumentation Labsys™ DTA/DSC was used for the measurements. Samples masses between 35-45 mg were used and the measurements were made at a heating rate of 5 K/min. To ensure good thermal contact the samples were packed in Al₂O₃ powder and did not touch the Al₂O₃ crucible wall. The reference crucible was also filled with Al₂O₃ powder, but contained no sample. During operation, the furnace was purged by high purity (99.998%) Ar gas to prevent significant oxidation up to the solidus. The DSC was calibrated in the temperature range of interest using Cu and Ag standards. This calibration was performed using masses of Cu and Ag that were comparable to the samples of interest and at the same heating rate as used for the measurements. Both standards had a purity greater than 99.99%.

Principle of Temperature Calibration

As stated earlier, the usual method of emissivity calibration is to match a measured temperature to that of a known heat signature. For ESL the calibration heat signatures are typically the transitions at the solidus or liquidus temperatures. Since the spectral emissivity is known to change with the surface phase of the sample [6–9], for liquid property
measurements the emissivity must be calibrated to the liquid phase. When the liquidus and solidus temperatures are separated, such as in a binary eutectic alloy, the heat of fusion is distributed across the two-phase liquid/solid region.

A simplified schematic of a binary eutectic phase diagram is shown in Fig. 2.1. The compositions numbered in Fig. 2.1.a correspond to the 1-eutectic composition, 2-a near eutectic composition, 3-an off eutectic composition and 4-the nearly pure element. The heat evolved at a given temperature, \( H \), is the latent heat of transition, \( L \), multiplied by the mass fraction of the sample transformed at that temperature. In differential form, this is described by

\[
dH(T)/dT = \chi_M (d\chi_M/dT),
\]

(2.5)

where the equilibrium mass fraction at a given temperature, \( \chi_M \) (the subscript \( M \) represents the mass), can be determined from the lever rule. An idealized view of the mass fraction of the liquid as a function of temperature for each composition is shown in Fig. 2.1.b. This only takes into account equilibrium conditions; in a true transformation the kinetics must also be considered, which will broaden in temperature the curves shown. Nevertheless, it serves as a useful model to extract some of the key features of the thermal signatures on transformation.

For all compositions, the mass fraction of liquid has a discontinuity on crossing the solidus temperature and a bend at the liquidus temperature. The resulting behavior in \( dH(T)/dT \) is a spike at the solidus temperature and step at the liquidus temperature. As the composition moves away from the eutectic composition, the discontinuity in the mass fraction at the solidus temperature decreases and the bend at the liquidus becomes more pronounced, as shown in Fig. 2.1.c. Since in DSC, \( dH(T)/dT \) is generated directly, the behavior shown in Fig. 2.1.c is that expected in DSC data for solid-liquid transformations, although features
will be broadened and shifted to higher temperature due to kinetic effects and finite heating rates.

In the ESL experiments, the samples are heated at constant power. Ignoring changes in the specific heat, the liquid mass fraction is expected to increase linearly with time, $dH(T)/dt \propto$
\( \frac{d\chi_M}{dt} \); this is shown schematically in Fig. 2.1.d. Near the eutectic composition \((i.e. \ 1 \text{ and } 2 \text{ in Fig. 2.1.a})\) a plateau will be observed in the time/temperature curve measured in ESL, which can be matched to the eutectic temperature. Far from the eutectic \((3)\) both the solidus (eutectic) and liquidus temperatures will be observed. The discontinuity in the mass fraction of the solid phase will still appear as a plateau upon heating, but in addition a strong inflection will be observed on heating through the liquidus. Near the pure element \((4)\) the fraction of liquid formed at the solidus will be small and not evident in ESL. Instead, the curvature near the liquidus temperature may be so extreme that the liquidus transformation will appear as a plateau.

With this understanding of the relationship between the temperature signatures observed in DSC and ESL, the temperature calibrations can be performed for compositions with separated liquidus and solidus temperatures, without having well-documented and accurate equilibrium phase diagrams.

**Uncertainty in Temperature due to Emissivity Calibration**

There are two primary contributions to the uncertainty in absolute temperature: signal noise and uncertainty in emissivity. The signal noise, derived from Eq. 2.3, sets the precision of the temperature measurement, which for a given signal, uncertainty scales as

\[
\frac{\Delta T_{\text{Noise}}}{T} = T \left( \frac{\Delta S_{\text{Noise}}}{S} \right),
\]

where \( \Delta \) denotes the uncertainty in the parameter. For the ratio temperature \( \Delta S_{\text{Noise}}/S \) is \( \sqrt{2} \) times the signal uncertainty of the individual colors, because the ratio contains the statistical errors of each single-color measurement. Since the scaling factor for the ratio measurement is also approximately \( 1/6^{\text{th}} \) of that of the constituent wavelengths \( (C_{1-\text{Color}}/C_{\text{Ratio}} = 6) \), the
precision of the ratio measurements is nearly nine times worse than that of a single color pyrometer.

The emissivity is a multiplication factor on the signal, therefore, the uncertainty in emissivity, \( \Delta \varepsilon \), propagates to the temperature with the same functional form as the signal error, Eq. 2.6. Treating the uncertainty in the noise and emissivity as independent errors gives the total uncertainty in the temperature measurement,

\[
\frac{\Delta T}{T} = \sqrt{\left( \frac{\Delta T_{\text{Noise}}}{T} \right)^2 + \frac{T^2}{C^2} \left( \frac{\Delta \varepsilon}{\varepsilon} \right)^2}. \tag{2.7}
\]

Away from the calibration point \( \Delta \varepsilon \) includes terms corresponding to the temperature dependence of the emissivity, \( \Delta \varepsilon (T) \sim \Delta \varepsilon (T_0) + d\varepsilon/dT (T - T_0) \). For a single wavelength the change in spectral emissivity in metallic alloys can be several percent over a range of 100 °C [10,11]. This can lead to a significant error far from the calibration point. Although ratio measurements suffer from poor precision they have an advantage in overall accuracy, due to a smaller temperature dependence of the emissivity ratio.

An expansion of the emissivity ratio with temperature for small differences in wavelength is described by

\[
\frac{\varepsilon (T, \lambda_2)}{\varepsilon (T, \lambda_1)} \sim \frac{\varepsilon (T_0, \lambda_2)}{\varepsilon (T_0, \lambda_1)} + \frac{2 (d\varepsilon (\lambda_2)/dT - d\varepsilon (\lambda_1)/dT)}{\varepsilon (T, \lambda_1) + \varepsilon (T, \lambda_2)} (T - T_0). \tag{2.8}
\]

The first term in Eq. 2.8 is set at the calibration temperature, \( T_0 \), while the pre-factor of the linear term indicates the slope of the emissivity ratio with respect to temperature. Calibrations of ratio pyrometers are valid over a wider temperature range than single wavelength pyrometers are, because if the emissivities of the two wavelengths vary similarly with temperature \( (d\varepsilon (\lambda_2)/dT \approx d\varepsilon (\lambda_1)/dT) \) their ratio will be temperature independent. This
cancellation is particularly critical for accurate measurements of the derivatives with respect to temperature (e.g. thermal expansivity), since the temperature dependence of the spectral emissivity can add significant error.

Even if the emissivity or emissivity ratio is not a function of temperature, the uncertainty in the emissivity at the calibration temperature propagates to measurements of the derivatives with respect to temperature. This is because the emissivity changes the temperature away from the calibration temperature in a nonlinear manner. For example, if the emissivity is constant in an arbitrary variable $x$ (i.e. $d\epsilon/dx = 0$), the fractional uncertainty in its derivative with respect to temperature for noise-free data is twice the fractional uncertainty of the temperature at the calibration point due to the uncertainty in the emissivity,

$$\left| \frac{\Delta dx/dT}{dx/dT} \right| = 2 \frac{T}{\epsilon} \left| \frac{\Delta \epsilon}{\epsilon} \right|. \quad (2.9)$$

The ratio pyrometer used in these experiments has an approximate temperature uncertainty of 0.75% (7 °C tolerance) at 900 °C, resulting in an uncertainty in the temperature derivative of 1.5% due to the propagation of this uncertainty through the emissivity.

### 2.1.3 Results

According to the equilibrium phase diagram [12] the compositions Cu$_{100-x}$Zr$_x$ transition from a line compound at $x = 50$ to an eutectic at $x = 44.5$. The solidus temperature across this compositional range is expected to be 916 °C, as shown in Fig. 2.2.a. As expected, DSC measurements (Fig. 2.2.b) show peaks corresponding to the liquid and solidus temperatures in this compositional range (see Fig. 2.2.a). The liquidus temperature could not be determined for Cu$_{55}$Zr$_{45}$ because the DSC peak corresponding to the solidus transition was too
weak and broad. Although there is some systematic disagreement in the measured solidus temperatures, the liquidus/solidus features observed in the DSC match those in the reported phase diagram to within the uncertainty of the measurements, ± 5 °C. This uncertainty in the calibration temperature results in a 0.5% uncertainty in the ratio pyrometer emissivity calibration.

Figure 2.2: Liquidus and solidus transitions, (a) as a function of composition across the Cu$_{100-x}$Zr$_x$ $x =45$-50 from the equilibrium phase diagram (adapted from [12], solid lines) and from DSC measurements (solidus △ and liquidus ■), and (b) observed by heat-flow measurements, background subtracted and normalized to sample mass.

In ESL the temperature versus time profiles obtained during heating from the solid at constant power show the expected two-plateau heat signatures corresponding to the liquidus and solidus transitions (Fig. 2.3).

All compositions were calibrated to the solidus temperature (916 °C), although the liquidus temperatures also matched those expected from the DSC measurements, validating
Figure 2.3: Liquidus and solidus transitions observed in ESL for Cu$_{100-x}$Zr$_x$ ($x = 45, 48, 49, 50$) alloys; the time axis is normalized to match the onset and completion of the solid-liquid transitions.

the overall method. No features were observed due the surface emissivity change upon melting, indicating that the ratio pyrometer calibration is reliable in both the liquid and solid phases. It is interesting to note that in the Cu$_{50}$Zr$_{50}$ composition a small signature that was consistent with crossing the solidus was observed during heating, both in the DSC and the ESL. The temperature of this heat signature is consistent with a compositional shift of the Cu$_{50}$Zr$_{50}$ sample to higher Cu. This is likely be the result of some Zr segregation to an Oxygen-stabilized intermetallic phase (e.g. Zr$_2$Cu$_{(1-x)}$O$_x$), such has been reported in ZrTiCuNiAl alloys [13–15].

Upon cooling, two recalescence events are observed for the three alloy compositions shown in Fig. 2.4. As already noted the emissivity calibration changes minimally between phases, indicating these are real features in the temperature profile. During the first recalescence
the temperature is increased to between the liquidus and solidus temperatures, as the solid phase grows from the supercooled liquid. The first crystallization proceeds rapidly, with the heat evolved balancing the radiated heat loss. With continued transformation, the rate of crystallization slows down as the solid approaches its equilibrium fraction and the sample temperature begins to decrease, noted by the rounded shape of the crystallization plateau. That the temperature as a function of time during this first crystallization is a mirror to that during the heat-up, indicates that the mass fractions of liquid and solid in the sample must be very nearly in equilibrium at each temperature above the solidus. For all three alloys, the primary solidification phase should be Cu$_{50}$Zr$_{50}$. With the argued shift to higher Cu in the Cu$_{50}$Zr$_{50}$ liquid due to the presence of oxygen, partitioning within the liquid phase would be required for all three alloys, moving the composition towards that of the eutectic at 44 at.% Zr. The second recalescence, then, likely corresponds to the crystallization of the remaining liquid to the Cu$_{10}$Zr$_{7}$ phase.

![Figure 2.4: Liquidus and solidus transitions observed in ESL upon heating and cooling for (a) Cu$_{50}$Zr$_{50}$, (b) Cu$_{51}$Zr$_{49}$ and (c) Cu$_{52}$Zr$_{48}$.](image-url)
2.1.4 Concluding Remarks

From the error propagation of the uncertainty in emissivity for optical pyrometer measurements to the temperature and derivatives with respect to temperature, it is clear that accurate thermal calibration is required for reporting quality thermophysical property measurements. The use of DSC measurements to calibrate the optical pyrometers widely used in levitation experiments is outlined and applied to four Cu-Zr compositions near and away from a eutectic composition. The heat signatures observed in the DSC measurements show good agreement with the temperature of transformation features reported in the phase diagram. Peaks and discontinuities observed in the DSC measurements were reflected in plateaus and curves in the ESL temperature-time profiles, which trended as expected across composition. For systems in which phase diagram information is unavailable, this method of temperature calibration provides a valuable tool for the correlation of temperature with thermophysical property measurements and phase transition studies.

2.2 Containerless Measurements of Density and Viscosity for a Cu$_{48}$Zr$_{52}$ Liquid [16]

2.2.1 Introduction

The Cu-Zr alloys are of intense interest to the metallic glass community as a simple binary system in which multiple bulk metallic glasses have been reported [17–20]. Glass formability
is, however, very sensitive to alloy composition. For example, Cu$_{50}$Zr$_{50}$ has a critical casting thickness for glass formation of over 1 mm [17, 20], while two atomic percent away, at Cu$_{48}$Zr$_{52}$, the critical casting thickness drops by 30% [20]. Density and viscosity data are necessary for building an understanding of this sensitivity to composition. However, the high reactivity of these metallic liquids makes measurements of these properties difficult and can result in widely varying reports. Containerless measurements techniques, such as electrostatic levitation (ESL) [1,21–23] or micro-gravity electro-magnetic levitation (EML) [24–26], provide the best way to process the alloys and make the desired measurements. In this section, density and viscosity data are reported in both equilibrium and supercooled liquid Cu$_{48}$Zr$_{52}$ with descriptions of the measurements as performed in the WU-BESL.

2.2.2 Experimental Apparatus and Procedures

2.2.2.1 Specimens and Their Purities

The Cu$_{48}$Zr$_{52}$ sample was prepared using high-purity Cu (99.995%) and Zr (99.9+% with nominal 3% Hf) by arc-melting on a water-cooled Cu hearth in a high-purity Ar gas atmosphere (99.998%). The arc-melting chamber was evacuated at least three times to less than 100 mTorr and backfilled with Ar gas. A Ti-Zr getter located near the sample material was kept molten for about one minute to further reduce residual oxygen before melting the sample material. Initially, an approximately one gram master ingot was prepared from the constituent elements and melted three times to ensure a homogeneous composition; the ingot was discarded in case the mass loss exceeded 0.05%. The 77.05 mg ESL sample was made by re-melting a portion of the master ingot. Any mass loss in this step was less than the measurement error.
2.2.2.2 Description of Experimental Technique

Apparatus

ESL was used to study the high temperature liquids in a containerless, vacuum environment. In the recently constructed Washington University Beamline ESL, or WU-BESL [4], inductively charged samples (2.0 to 4.0 mm diameter) are levitated in an electrostatic field (0 to 2 MV/m) under high vacuum (~10^{-7} Torr). Charge is maintained during processing by an external UV source, while the sample position is maintained by three pairs of orthogonal electrodes and a control algorithm [27].

Measurement and Control of Temperature

The temperature was measured using a two-color Process Sensors Metis MQ22 pyrometer, having a range of 873 to 2573 K and effective wavelengths at 1.40 and 1.64 μm. The sample temperature is controlled with a 980 nm 50W nlight Pearl\textsuperscript{TM} Model P4-050-0980-AIM diode laser. For calibration, the pyrometer reading at the end of the liquidus curve observed in ESL was matched to the temperature of the liquidus measured by differential scanning calorimetry (Labsys\textsuperscript{TM} DTA/DSC, Setaram Instrumentation), which is 1223 ± 5 K.

Measurement of Sample Volume

Figure 2.5 shows a diagram of the volume measurement system. Video data are obtained from the levitated sample using a 1.3 Megapixel Gig-E CMOS pixeLINK Monochrome Camera. As shown, the sample is backlit by a collimated microscope that is illuminated by a 590 nm LED. A narrow-band-pass filter of 590 nm ± 10 nm FWHM is placed just after a K2/SC Long Distance Video Microscope, which has a close-focus objective capable of magnifications of
2.13X-0.71X and a working distance of 222-418 mm. The band-pass filter is used to exclude interference from thermal radiation from the sample in the measured images [28]. The video data were acquired at a rate of 25 frames per second (fps) with an exposure time of 0.65 ms. The pixel dimensions were calibrated before sample measurement using 3/32 diameter (tolerance $\pm 3\times10^{-5}$”) grade-3 tungsten carbide standards (Industrial Tectonics Inc.). Due to the high vapor pressure of copper, the maximum temperature of the liquid was confined to less than 300 K above the liquidus temperature to minimize sample evaporation.

![Figure 2.5: Schematic diagram showing the volume measurement system in WU-BESL.](image)

The sample volume, and consequently the density $\rho$, was determined by analyzing frames from video of the shadow of the backlit, levitated sample. A typical video frame is shown Fig. 2.6.a. The 2d edges of the shadow were first obtained following a modified version of the algorithm described by Bradshaw et al. [29]. This is a threshold algorithm, for which an edge location is defined as the point on a line profile where the intensity (interpolated pixel values) attains some threshold value. In the Bradshaw algorithm, the threshold is constant for all edges and is calculated as halfway between that of the average background intensity and the average shadow intensity. Using a cubic interpolation between pixel values, this threshold can be located to within sub-pixel resolution along line profiles in the image. With the edge locations, the centroid, axis of symmetry and Legendre coefficients of the shadow are fit and the volume is determined by integrating about the axis of symmetry. Although a precision of 0.0265% is reported by Bradshaw et al., the authors noted that nonuniformity in
the background intensity may impact the quality of measurements [29]. This non-uniformity in the background intensity is shown in Fig. 2.6.b, for the line profile indicated on Fig. 2.6.a.

Figure 2.6: (a) A video image of the grade 3 tungsten carbide calibration standard. (b) A line profile of the image measured along the sample vertical axis. The detected edges at the top (c) and bottom (d) of the image assuming an average background intensity (red △) or an edge-specific background (blue □).

By assuming a single average threshold on an inhomogeneous background, the edge locations are artificially pushed toward darker regions and away from lighter regions, as shown in Fig. 2.6.c and 2.6.d. Although the effect partially cancels, the calculated volume was observed to change by 0.01% between the assumptions of a constant threshold algorithm and an edge-specific background. An edge-specific background accounts for the inhomogeneity, by calculating a new threshold intensity for each edge. In this modification, the edge specific
threshold is defined as halfway between the shadow and background intensities along the edge’s line profile. A modified algorithm that includes this correction is as follows.

As in the Bradshaw algorithm, a coarse method of edge detection is used to define a candidate area of 21x21 pixels around the silhouette edges before sub-pixel methods are used. This mask creates an annulus within which the edges can found. In the modified algorithm a second, larger, annulus is defined that encompasses the range of sample motion within all of the video frames. This annulus is given an outer radius and an inner radius that are identified as twice and one-tenth the approximate sample radius, respectively. When line profiles are taken to detect the edges, the pixels located outside the candidate area but within the outer edge of the second annulus, are averaged to refine the background intensity along that search direction. The same procedure can be followed between the inner radius and candidate area to redefine the sample intensity. However, in practice there should be no inhomogeneity within a silhouette, so that only the edge-dependent background intensity defines the new threshold. Using the edge-dependent threshold, pixel values are interpolated with a cubic polynomial to determine the location of the edge. As in the Bradshaw algorithm, the centroid and Legendre coefficients of the shadow are fit and the volume is obtained by integrating about the axis of symmetry. In the modified algorithm, the axis of symmetry is not fit; instead, the optical equipment is leveled before measurements are made. Since sample deformation of the liquid primarily results from gravitational effects, the symmetry axis will be vertical. In solids, where the axis of symmetry may not be along the vertical axis, this simplification removes a free parameter from the volume calculation and, therefore, has been observed to reduce the scatter in the volume measurements.

During ESL operation, the density video data are acquired during radiative free-cooling, which gives the best sample stability. The data obtained from multiple radiative cooling
measurements, such as the one shown in Fig. 2.7, are averaged to give the density as a function of temperature, allowing the thermal expansion coefficient to be determined. The uncertainty in the absolute measurement of liquid density is dominated by the uncertainty in the calibration from pixels to SI units, ≈ 0.1% tolerance. The accuracy of the thermal expansion is composed of both the uncertainty in the fits to the density as a function of temperature, ≈ 1% to 95% confidence, and the propagated uncertainty from the temperature calibration to the data, ≈ 1% tolerance. In the solid phase the sample shape becomes asymmetric due to shrinkage, faceting, and grain growth upon crystallization. The large amount of scatter after recalescence (Fig. 2.7) reflects sample rotation. By binning the solid phase data at a period of one half the sample rotational frequency, the scatter in the solid phase density can be reduced to the same order as that of the liquid phase. Each bin is treated as an independent measurement for purposes of error propagation.

**Measurement of Viscosity**

In ESL the viscosity, \( \eta \), is measured using the oscillating drop technique, for which surface vibrations are driven in liquids by modulating the levitation field near a resonant frequency. When the driving signal is stopped the surface vibrations follow the behavior of an underdamped simple harmonic oscillator, *i.e.* an exponentially decaying oscillation, at a frequency that is independent of the driving frequency. This resonant frequency is determined by the surface tension, while the viscosity dictates the decay time. Due to the sensitivity of the surface tension to the partial pressure of oxygen [30–32], only viscosity measurements are reported in this section.

The formula for the decay of the \( n \)th surface harmonic was derived by Lamb in 1881 [33] and is shown in Eq. 2.10, where \( a \) is the radius of the spherical sample, \( \rho \) is the density and
Figure 2.7: The temperature and measured density during radiative free-cooling for a Cu$_{48}$Zr$_{52}$ liquid (before recalescence) and for the solid (after recalescence). The scatter is much greater for the solid.

η is viscosity of the sample.

\[
\tau_n = \frac{\rho a^2}{\left[(n - 1) (2n + 1) \eta\right]} \tag{2.10}
\]

By modulating the levitation field near resonance the \(n = 2\) mode gains amplitude, which, after the driving force is removed, decays exponentially with time. To monitor the changing surface of the sample, 50% of the power from the collimated positioning LED is split and reflected into the viscosity camera, as shown in Fig. 2.8. The viscosity camera used is a 1.3 Megapixel Gigabit-Ethernet CMOS pixeLINK monochrome camera (the same as the one
used for the density measurements) with a KOWA lens for focusing. In other ESL systems, the magnitude of the second surface harmonic is detected either from an analysis of high resolution-high speed video [30] or by photo-detectors sensitive to changes in the second harmonic [1, 23]. WU-BESL uses a low cost hybrid of these two techniques, with a low resolution-high speed video (∼1700 fps) serving as the photo-detector.

Figure 2.8: Schematic diagram showing the light sources and sensor used for the viscosity measurements in WU-BESL.

Since the liquids are axially symmetric in the electric field, the radius function defining the sample shape can be expanded in a series of symmetric Legendre polynomials (m = 0),

\[ r(\theta) = \sum_{n=0}^{\infty} a_n P_n(\cos(\theta)). \]

\[
\begin{align*}
A &= \frac{1}{2} \int_{-\pi}^{\pi} r^2 d\theta \\
&= \frac{1}{2} \int_{-\pi}^{\pi} \left( a_0 + \frac{a_2}{2} (3\cos^2(\theta) - 1) \right)^2 d\theta \\
&= \pi a_0^2 + a_0 a_2 \pi/2 + 11 a_2^2 \pi/32. \\
\end{align*}
\]

For small perturbations, the \( a_2^2 \) term is infinitesimal compared to \( \pi a_0^2 + a_0 a_2 \pi/2 \). Although any sample deformation results in a larger surface area, Eq. 2.11 indicate that the cross-sectional area of the sample decreases with sample compression and increases with elongation, as shown in Fig. 2.9. Therefore, an intensity summation can be used as a measurement
of the second harmonic, rather than relying on the complex edge fitting used in volume measurements. By using automated data acquisition, 148 measurements of the intensity as a function of time, like those shown in Fig. 2.10.a, were acquired during a 20 minute period. Approximately one-third of these measurements were rejected due to poor signal-to-noise, or non-axial modulation.

![Figure 2.9: Shadows of an oscillating drop at (a) positive amplitude (b) zero amplitude and (c) negative amplitude of the second surface harmonic.](image)

The analysis of the intensity signals was also automated to handle the large volume of data. The levitation voltage was recorded concurrently with the video, so that the un-driven signal could be identified. The un-driven signal reflects that of a damped simple harmonic oscillator, which has the functional form [21]

\[
S(t) = A \exp(-t/\tau) \sin(2\pi f_0 t + \phi). \tag{2.12}
\]

The experimental signal includes the baseline curvature, low frequency oscillations and noise. A high pass filter applied to the Fourier transform was used to remove baseline curvature before making any analysis. To minimize unnecessary distortion of the area signal (which can lead to systematically lower damping constants), only frequencies with periods longer than twice the range of data were filtered.
Figure 2.10: Representative intensity profile (a) as measured from video files and (b) truncated to optimize the signal-to-noise (data range bracketed by dashed lines in (a)). The non-linear fit to the frame intensities (■) for the resonant frequency and damping constant determination is shown in (b) (solid red curve).

As shown in Fig. 2.10.a, more data are acquired than can be resolved outside of the background noise. If the full data set is used, fits of the form of Eq. 2.12 tend toward systematically higher frequencies and longer damping times. The signal-to-noise becomes unfavorable when the signal decays to approximately 10% of the original amplitude, which is twice the damping constant. To determine this optimal data range, the process for determining the damping constant followed by a truncation of the data range was iterated until convergence. The signal, truncated to the optimized range, was fit using a non-linear Levenberg-Marquardt algorithm to Eq. 2.12 (shown in Fig. 2.10.b) to obtain the frequency and damping data.

2.2.3 Results

The measured density of liquid and solid Cu_{48}Zr_{52} as function of temperature for three radiative cooling experiments is shown in Fig. 2.11. At the liquidus temperature, 1223 K,
the density of the liquid is $7.032 \pm 0.007 \text{ g cm}^{-3}$ and the density of the solid extrapolated to that temperature is $7.166 \pm 0.008 \text{ g cm}^{-3}$, indicating a change in density of $1.869\pm0.001 \%$ upon crystallization. The thermal expansion coefficients, $-d \ln \rho/dT$, at 1223 K are $6.4 \pm 0.1 \times 10^{-5} \text{ K}^{-1}$ for the liquid and $3.5 \pm 0.3 \times 10^{-5} \text{ K}^{-1}$ for the solid.

Figure 2.11: Density as a function of temperature for liquid and solid Cu$_{48}$Zr$_{52}$.

The measured viscosity as a function of temperature is shown in Fig. 2.12. The functional form of the viscosity is well described by

$$A \exp\left[\left(E_0 + E_1 \left(1/T - 1/T_0\right)\right) \times \left(1/T - 1/T_0\right)\right], \quad (2.13)$$
where $T_0 = 1223$ K, $A = 0.025404$ Pa·s, $E_0 = 8437.85$ K and $E_1 = 16901356$ K$^2$. This functional form for the viscosity may be viewed as an Arrhenius form with a temperature-dependent activation energy. The temperature dependence of the activation energy indicates a transition from a high temperature free-diffusion to more restrictive flow between states on the energy landscape [34].

### 2.3 References

http://link.aip.org/link/?RSI/64/2961/1


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[34] P.G. Debenedetti, F.H. Stillinger, Nature 410(6825), 259 (2001). DOI 10.1038/35065704. URL http://dx.doi.org/10.1038/35065704
Chapter 3

Analysis of Diffraction Measurements in Beamline Electrostatic Levitation

In addition to thermophysical property measurements, the WU-BESL was designed for transport to the Advanced Photon Source at Argonne National Laboratory for in situ diffraction studies of supercooled liquid phases [1]. As will be discussed, the sample geometry for these experiments is not commonly encountered in crystallography and, consequently, the corrections specific to a small, misaligned beam incident on a spherical sample have not previously been reported. In Sect. 3.1, the absorption and secondary corrections specific to this geometry, which are valid for all levitation experiments, are derived [2]. To incorporate these equations and other relevant corrections, and to improve data reduction times for WU-BESL measurements, a LabVIEW™ analysis program was developed. Verification of these analysis methods and details of the corrections appropriate for levitation geometries are described in Sect. 3.2 [3]. The manual for the LabVIEW™ software, X-ray Batch.vi, can be found in the Appendix C. At the time of this writing, Sect. 3.1 is published in Acta Crystallographica Section A [2] and Sect. 3.2 is under review with the Journal of Applied Crystallography [3].

3.1.1 Introduction

Levitation techniques, including electrostatic levitation, electromagnetic levitation and conical nozzle levitation, have been developed for the study of liquids in an inert, contactless environment. The absence of a container removes a major source of heterogeneous nucleation and allows studies of liquids in the supercooled state (i.e. below the equilibrium melting temperature). Recently, these levitation techniques have been used for laboratory X-ray, synchrotron, and neutron scattering studies of these supercooled liquids [1, 4–9]. Owing to surface-tension effects, the liquids are nearly spherical in shape. A transmission geometry is typically used for the scattering studies. In many cases, the beam size is smaller than the sample size, so that previously reported spherical corrections cannot be applied for the analysis of the data. Beam alignment becomes critical in these cases; off-axis transmission through the spherical samples can result in asymmetric scattering. Although precision alignment stages for levitation chambers have been reported [1], variations in sample size and density can cause positional variation between measurements. Some method for correcting for the resulting asymmetric scattering is needed to compare measurements.

Secondary scattering and absorption corrections for standard geometries (i.e., plane sample reflection [10,11], transmission [11] and moving sample transmission [12] as well as cylindrical sample transmission [13,14]) are well known. Although absorption corrections for small-
and large- [16] diameter X-ray beams incident on spherical samples have been reported, neither secondary scattering corrections nor absorption corrections for off-axis transmission through spherical samples have ever been previously reported. These corrections are presented in this section, giving the integral forms of absorption and secondary scattering intensity through a given solid angle by an amorphous spherical sample from an off-axis, infinitesimal, partially polarized X-ray beam. An analytic approximation is also reported for the absorption correction in the small-angle limit for rapid computation.

### 3.1.2 Theory

The theory for X-ray absorption and secondary scattering correction for arbitrary sample shapes, for the transmission geometry shown in Fig. 3.1, is derived in this section. For notation used in this section, see Table 3.1.

![Figure 3.1: Transmission geometry viewed in different magnifications: (a) at differential volume length scales, (b) at sample length scales, and (c) detector length scales.](image-url)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_0$</td>
<td>Intensity of the principal beam incident on the sample</td>
</tr>
<tr>
<td>$I_i$</td>
<td>Intensity of a beam after the $i$th scattering event</td>
</tr>
<tr>
<td>$\sigma_e$</td>
<td>Differential electron scattering cross section</td>
</tr>
<tr>
<td>$P(\kappa, 2\theta, \phi)$</td>
<td>Angle-dependent attenuation due to polarization</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Polarization, defined as $(I_x - I_y) / (I_x + I_y)$</td>
</tr>
<tr>
<td>$J(2\theta)$</td>
<td>First order scattering intensity in electron units</td>
</tr>
<tr>
<td>$n$</td>
<td>Number density</td>
</tr>
<tr>
<td>$V$</td>
<td>Ideal, unattenuated scattering volume</td>
</tr>
<tr>
<td>$V'$</td>
<td>Effective scattering volume due to attenuation</td>
</tr>
<tr>
<td>$dV_1$</td>
<td>Differential volume of the principal beam path, $dV_1 = dA_0 dr_0$</td>
</tr>
<tr>
<td>$dV_2$</td>
<td>Differential volume of the primary scattered beam path, $dV_2 = r_1^2 \cos (2\theta_1) d\phi_1 d2\theta_1 dr_1$</td>
</tr>
<tr>
<td>$dA_0$</td>
<td>Principal beam differential area $dA_0 = r'dr'd\phi'$</td>
</tr>
<tr>
<td>$\phi', r'$</td>
<td>Principal beam azimuthal and radial coordinates</td>
</tr>
<tr>
<td>$r_s$</td>
<td>Sample and beam radii</td>
</tr>
<tr>
<td>$r_B$</td>
<td></td>
</tr>
<tr>
<td>$\xi, \rho, z$</td>
<td>Azimuthal and radial coordinates defining a distance from the central axis of a spherical sample, and the coordinate along the central axis</td>
</tr>
<tr>
<td>$\xi_0, x$</td>
<td>Azimuthal and radial coordinates defining beam center incidence on spherical sample</td>
</tr>
<tr>
<td>$R$</td>
<td>Geometry- and angle-dependent path length from the final diffraction event to the edge of the sample</td>
</tr>
<tr>
<td>$\mu, \mu'$</td>
<td>Linear attenuation coefficient of the scattering material before and after energy shift due a diffraction event</td>
</tr>
<tr>
<td>$R$</td>
<td>Total scattering vector</td>
</tr>
<tr>
<td>$r, \phi, 2\theta$</td>
<td>Spherical coordinates of total scattering</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Vector path of the beam following the $i$th scattering event</td>
</tr>
<tr>
<td>$r_i, \phi_i, 2\theta_i$</td>
<td>Diffraction coordinates of the $i$th scattering event</td>
</tr>
<tr>
<td>$O_i$</td>
<td>A point defined by the path $\sum_i R_{j-1}$</td>
</tr>
<tr>
<td>$\chi_i$</td>
<td>Atom fraction of element $i$</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>Atomic number of element $i$</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Molar mass of element $i$</td>
</tr>
<tr>
<td>$(\mu/n)_i$</td>
<td>Mass absorption coefficient of element $i$</td>
</tr>
<tr>
<td>$f_i$</td>
<td>Atomic form factor of element $i$</td>
</tr>
<tr>
<td>$i(M)$</td>
<td>Incoherent scattering of element $i$</td>
</tr>
<tr>
<td>Subscript 's'</td>
<td>For any defined variable $\alpha$, subscript 's' denotes a change in scale to units of sample radius such that $\alpha/r_s = \alpha_s$</td>
</tr>
</tbody>
</table>
As shown in Fig 3.1.a the infinitesimal scattered intensity \( dI(r, 2\theta, \phi) \) at some distance \( r \) from an infinitesimal scattering volume \( dV \) is given by

\[
dI(r, 2\theta, \phi) = I_0 \frac{\sigma_e n}{r^2} P(\kappa_0, 2\theta, \phi) J(2\theta) dV, \tag{3.1}
\]

where \( n \) is the average number density of scattering element, \( I_0 \) is the intensity of the principal beam incident on the volume and \( P(\kappa_0, 2\theta, \phi) \) accounts for polarization effects. The first-order scattering intensity \( J(2\theta) \) is a combination of the coherent and incoherent scattering intensity in electron units. Since the coherent and incoherent electron cross sections are approximately equal, \( \sigma_e \) is the differential Thomson cross section for electrons, \( e^4/m^2c^4 \).

Since only amorphous samples are considered, \( J(2\theta) \) is assumed to be symmetric about the azimuthal angle \( \phi \). In this case, scattering asymmetry arises from polarization effects, \( P(\kappa, 2\theta, \phi) \), which are described by

\[
P(\kappa, 2\theta, \phi) = \frac{1}{2} + \kappa \left[ \sin^2(\phi) - \cos^2(\phi) \right] / 2 + \left\{ 1 + \kappa \left[ \cos^2(\phi) - \sin^2(\phi) \right] \right\} \cos^2(2\theta)/2, \tag{3.2}
\]

where \( \kappa \) quantifies the polarization by the ratio of difference in intensity between the \( x \) and \( y \) components of the incident beam and the total intensity \( (I_x - I_y) / (I_x + I_y) \) \[17, 18\].

Far from the scattering event (Fig. 3.1.c), the intensity measured at a solid angle, defined by \( 2\theta \) and \( \phi \), is the integral of Eq. 3.1 over the scattering elements in the sample. The total number of scattering elements is the integral of Eq. 3.1 over the volume \( V \) for a homogeneous sample. For a non-absorbing material this intensity would be described by

\[
I(r, 2\theta, \phi) = \frac{I_0 n}{r^2} \sigma_e P(\kappa_0, 2\theta, \phi) J(2\theta) V. \tag{3.3}
\]
In reality, both the intensity of the incident beam and the scattered beam are attenuated as they travel through the material according to Beer’s law, \( I(r) = I(0) \exp(-\mu r) \), where \( I(r) \) is the intensity a distant \( r \) into a material of attenuation coefficient \( \mu \). The first scattering intensity, accounting for this absorption, is given by Eq. 3.4, where, as shown in Fig. 3.1.b, \( r_0 \) is the path length of the incident beam to the differential scattering volume and \( R \) is the position and solid angle dependent path length of the scattered beam,

\[
I_1(r, 2\theta, \phi) = \left( I_0 n \sigma_e / r^2 \right) \int \int \int dV
\times \{ P(\kappa_0, 2\theta, \phi) J(2\theta) \exp[-\mu r_0 - \mu' R(\Omega)] \}.
\]

Equation 3.4 can be rewritten in the form of Eq. 3.3 by defining an effective scattering volume of the system as \( V' = \int \int \int \exp[-\mu r_0 - \mu' R(\Omega)] dV \). Absorption corrections convert the measured effective scattering volume to that for the non-absorbing case by multiplying Eq. 3.4 by a factor of \( V/V' \).

The scattered beam may, of course, continue to scatter within the sample. However, since each successive scattering event is less intense, only secondary scattering needs to be considered as a correction to recover the primary scattering intensity. A secondary scattering event is illustrated in Fig. 3.2, where an incident X-ray beam of intensity \( I_0 \) travels along the path \( R_0 \).

As previously noted, absorption will cause the beam to be attenuated along \( R_0 \), so that the intensity at the point \( O_1 \), where the beam is scattered, is given by

\[
I_0(O_1) = I_0 \exp(-\mu r_0),
\]
where $|\mathbf{R}_0| = r_0$. The first scattered beam may either take a direct path $\mathbf{R}$ to the detector (point $O_3$) or reach the detector after having a secondary scattering event at $O_2$. The contribution of the primary scattering intensity from the differential volume at point $O_1$ is $dI_1(\mathbf{R})$ at point $O_3$. For a small sample far from the detector, the integral over parallel rays at angles $2\theta$ and $\phi$ is the total primary scattering intensity at point $O_3$.

The intensity of the beam at $O_2$, scattered from $O_1$ and traveling a distance $\mathbf{R}_1$, is given by Eq. 3.6, where $dV_1$ is the differential scattering volume at point $O_1$, and $\kappa_0$ is the polarization state of the incident beam. If the scattering is inelastic, the absorption coefficient, $\mu'$, will differ from the original one. Since the change in energy is assumed to be small, for these calculations $\mu'$ can be set equal to $\mu$.

$$dI_1(\mathbf{R}_0, O_2) = I_0(O_1) P(\kappa_0, 2\theta_1, \phi_1)$$
$$\times \exp \left( -\mu' r_1 \right) \frac{n}{r_1^2} \sigma_e J(2\theta_1) dV_1$$

(3.6)
To be detected at point \( O_3 \), the beam must again scatter at \( O_2 \) so that it follows path \( R_2 \). The differential intensity of the secondary scattered beam measured at \( O_3 \) is described by Eq. 3.7. The beam leaves the sample at some point along the path \( R_2 \), but may also be attenuated by intermediate material (i.e. exit window and air path); the changing attenuation coefficients along the path are represented as a path integral in the exponential argument,

\[
dI_2 (R_0, R_1, O_3) = \left( I_0 n^2 \sigma_e^2 / r_1^2 r_2^2 \right) \exp \left[ -\mu (r_0 + r_1) - \int_{O_2}^{O_3} \mu(x)dx \right]
\]

\[
\times P (\kappa_0, 2\theta_1, \phi_1) J (2\theta_1) P (\kappa_1, 2\theta_2, \phi_2) J (2\theta_2) dV_1 dV_2.
\]

(3.7)

The first differential volume, \( dV_1 \), is the differential area of the principal beam, \( dA_0 \), multiplied by the differential path length \( dr_0 \), i.e. \( dV_1 = dA_0 dr_0 \). The second differential volume, \( dV_2 \), is described in terms of the diffraction coordinates of \( R_1 \) by \( dV_2 = r_1^2 \cos(2\theta_1) d\phi_1 d2\theta_1 dr_1 \).

From Fig. 3.2, the angles \( 2\theta_2 \) and \( \phi_2 \) describe the diffraction angles of the secondary scattering event.

For \( |R_2| >> |R_1| \) (far detector limit), \( R \approx R_2 \), so that the secondary diffraction angles \( 2\theta_2 \) and \( \phi_2 \) map onto \( R \) by a \( 2\theta_1 \) rotation about the \( y \)-axis and then a \( \phi_1 \) rotation about the
The rotation matrix, Eq. 3.8, constrains $2\theta_2$ and $\phi_2$, as shown in Eqs. 3.9 and 3.10,

\[
\begin{bmatrix}
\sin (2\theta_2) \cos (\phi_2) \\
\sin (2\theta_2) \sin (\phi_2) \\
\cos (2\theta_2)
\end{bmatrix}
\begin{bmatrix}
\cos (2\theta_1) \cos (\phi_1) & \cos (2\theta_1) \sin (\phi_1) & -\sin (2\theta_1) \\
-\sin (\phi_1) & \cos (\phi_1) & 0 \\
\sin (2\theta_1) \cos (\phi_1) & \sin (2\theta_1) \sin (\phi_1) & \cos (2\theta_1)
\end{bmatrix}
\begin{bmatrix}
\sin (2\theta) \\
\sin (2\theta) \cos (\phi) \\
\cos (2\theta)
\end{bmatrix},
\]

\[
\cos (2\theta_2) = \sin (2\theta_1) \cos (\phi_1) \sin (2\theta) \cos (\phi)
+ \sin (2\theta_1) \sin (2\theta) \sin (\phi)
+ \cos (2\theta_1) \cos (2\theta),
\]

\[
\tan (\phi_2) = [\cos (\phi_1) \sin (2\theta) \sin (\phi) - \sin (\phi_1) \sin (2\theta) \cos (\phi)]
\times [\cos (2\theta_1) \cos (\phi_1) \sin (2\theta) \cos (\phi)
+ \cos (2\theta_1) \sin (\phi_1) \sin (2\theta) \sin (\phi)
- \sin (2\theta_1) \cos (2\theta)]^{-1}.
\]

The angle $\phi_2$ only comes into the spherical geometry calculation through the secondary diffraction polarization term $P(\kappa_1, 2\theta_2, \phi_2)$. After the first scattering event, the polarization state of the beam changes, such that $\kappa_1$ is given by

\[
\frac{[\kappa_0 \cos^2 (\phi_1) - \kappa_0 \sin^2 (\phi_1) + 1] (\cos^2 (2\theta_1) + 1) - 2}{[\kappa_0 \cos^2 (\phi_1) - \kappa_0 \sin^2 (\phi_1) + 1] (\cos^2 (2\theta_1) - 1) + 2}. 
\]
Equation 3.7 is integrated over the volume of irradiated material for both the incident and primary scattered beams to obtain the total secondary scattering intensity at $O_3$. The differential intensity is described by Eq. 3.7, but it should be noted that the bounds on the integral are geometry dependent.

By convention [10, 12, 16], the ratio of secondary to primary scattering is reported in the form of Eq. 3.12, where $Q_M$ is the geometry dependent integral, which can be solved given $\mu t, 2\theta, \phi$ and $J(2\theta) / (\sum \chi_i Z_i^2)$, and summations are performed over elemental species $i$,

$$\frac{I_2}{I_1}(2\theta, \phi) = \frac{(\sum \chi_i Z_i^2)^2 Q_M}{J(2\theta) \sum \chi_i M_i (\mu/\rho)_i}. \tag{3.12}$$

### 3.1.3 Absorption for Off-Central Axis Beam

For a beam of cross-sectional area $dA_0$ that is incident off-center by a radial distance $x$ and at the angle $\xi_0$ onto a sample of radius $r_s$, the scattering volume is a triple integral over the area of the beam (beam radius and angle) and the sample thickness, as shown in Fig. 3.3.

The effective scattering volume for a spherical sample in this case is described by Eq. 3.13, where $R(r_0, 2\theta, \phi, \rho, \xi)$ is the position-dependent travel length of the diffracted beam and $dA_0(\phi', r')$ is the differential area of the principal beam,

$$V'_{\text{Sphere}}(2\theta, \phi) = \int \int dA_0(\phi', r') \left( \int \sqrt{r_s^2 - \rho^2} \, dr_0 \right) \times \exp \left[ -\mu r_0 - \mu \sqrt{r_s^2 - \rho^2} - \mu R(r_0, 2\theta, \phi, \rho, \xi) \right]. \tag{3.13}$$

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The function $R(r_0, 2\theta, \phi, \rho, \xi)$ can be obtained from the intersection between a cone centered at the origin pointing in the $+z$ direction and a sphere shifted by a distance $r_0$ along the $z$-axis and centered in the $x$-$y$ plane an angle $\xi$ from the $x$-axis and radial distance $\rho$, as shown in Fig. 3.4. The path length from the position $r_0, \rho, \xi$ to the surface of a sphere along the solid angle $2\theta, \phi$ is described by

$$R(r_0, 2\theta, \phi, \rho, \xi) = \rho \sin(2\theta) \cos(\phi - \xi) - r_0 \cos(2\theta)$$

$$+ \left[ r_0^2 \cos^2(2\theta) - r_0^2 - \rho^2 + r_s^2 ight] + 2r_0\rho \cos(2\theta) \sin(2\theta) \cos(\phi - \xi)$$

$$+ \rho^2 \sin^2(2\theta) \cos^2(\phi - \xi) \right]^{1/2}.$$
Given any arbitrary beam shape and incidence, the effective scattering volume can be obtained by numerically integrating eqs. 3.13 and 3.14.

For a circular beam that is centered off of the central axis, Eq. 3.13 becomes Eq. 3.15 with the x-axis aligned such that \( \xi_0 = 0 \),

\[
V_{\text{Sphere}}'(2\theta, \phi) = \int_0^{r_0} r' \, dr' \int_0^{2\pi} d\phi' \int_{-\sqrt{r_s^2 - \rho^2}}^{\sqrt{r_s^2 - \rho^2}} dr_0 \nonumber \\
\times \exp \left[ -\mu r_0 - \mu \sqrt{r_s^2 - \rho^2} - \mu R (r_0, 2\theta, \phi, \rho, \xi) \right],
\]

where \( \rho = \left\{ [r' \cos(\phi') + x]^2 + r'^2 \sin(\phi')^2 \right\}^{1/2} \), \( \xi = \tan^{-1} \left\{ r' \sin(\phi')/[r' \cos(\phi') + x] \right\} - \pi \), and \( r' \) and \( \phi' \) are beam coordinates.
It is useful to scale by units of the sample radius; here any scaled quantity is denoted by the subscript ‘s’ (e.g. $\alpha/r_s = \alpha_s$). This reduces the number of parameters from four ($\mu, r_B, r_s, x$) to three ($\mu r_s, r_s B, r_s x_s$) as shown in Eqs. 3.16 and 3.17,

$$V'_{Sphere} = r_B r_s^2 \int_{0}^{1} r_s' dr_s \int_{0}^{2\pi} d\phi' \int_{-\sqrt{1-\rho_s^2}}^{\sqrt{1-\rho_s^2}} dr_0s \times \exp\left[-\mu r_0s - \mu r_s \sqrt{1-\rho_s^2} - \mu r_s R_s (r_0s, 2\theta, \phi, \rho_s, \xi)\right],$$

(3.16)

$$R_s (r_0s, 2\theta, \phi, \rho_s, \xi) = \rho_s \sin (2\theta) \cos (\phi - \xi) - r_0s \cos (2\theta) + \left[r_0s^2 \cos^2 (2\theta) - r_0s^2 - \rho_s^2 + 1 \right. - 2r_0s \rho_s \cos (2\theta) \sin (2\theta) \cos (\phi - \xi) + \rho_s^2 \sin^2 (2\theta) \cos^2 (\phi - \xi) \right]^{1/2},$$

(3.17)

where $\rho_s = \left\{ [r_s' r_B \cos (\phi') + x_s]^2 + r_s'^2 (r_B)^2 \sin (\phi')^2 \right\}^{1/2}$ and

$$\xi = \tan^{-1} \left\{ r_s' r_B \sin (\phi') / [r_s' r_B \cos (\phi') + x_s] \right\} - \pi.$$

The integral in Eq. 3.16 has no closed-form solution. In the small beam limit, $r_B \to 0$, two of the integrals become trivial as shown by Eq. 3.18. The spherical correction can then easily be computed numerically,

$$V'_{Sphere} = \pi r_B r_s^2 \exp \left(-\mu r_s \sqrt{1-\rho_s^2} \right) \int_{-\sqrt{1-\rho_s^2}}^{\sqrt{1-\rho_s^2}} dr_0s \times \exp\left[-\mu r_0s - \mu r_s R_s (r_0s, 2\theta, \phi, x_s, \xi)\right].$$

(3.18)
If a numerical solution is too computationally expensive, such as when using fitting algorithms, an analytic expansion in the small-angle limit $2\theta \to 0$ may be used.

The asymptotic expansion of the absorption correction for a zero-width beam is given by Eq. 3.19, where the first six coefficients are specified in Table 3.2,

$$\frac{V}{V'} \sim \exp \left( \frac{2\mu r_s \sqrt{1-x_s^2}}{\sqrt{1-x_s^2}} \right) \times \sum_{i=0}^{\infty} A_i(\mu r_s, x_s, \phi) (2\theta)^i,$$

$$2\theta \to 0, r_{Bs} = 0.$$  

This correction must be applied to two-dimensional data since it can manifest itself as a large gradient in intensity across the detector. Although the higher-order terms in the $r_{Bs} \to 0$ expansion are valid corrections for $x_s + r_{Bs} < 1$, as parts of the beam miss the sample (i.e. for $x_s + r_{Bs} > 1$), these terms diverge from the numerical solution while the lowest order term remains accurate.
<table>
<thead>
<tr>
<th>( i )</th>
<th>( A_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>( \cos(\phi)\mu r_s x_s )</td>
</tr>
</tbody>
</table>
| 2     | \[
\frac{\mu r_s}{6(x_s^2-1)} \left[ 2\mu r_s \cos(\phi)^2 x_s^4 - x_s^2 \sqrt{1-x_s^2} \right. \\
\left. -2\mu r_s \cos(\phi)^2 x_s^2 + \sqrt{1-x_s^2} \right. \\
\left. -2x_s^2 \cos(\phi)^2 \sqrt{1-x_s^2} \right]
\] |
| 3     | \[
\frac{x_s \cos(\phi)\mu r_s}{6(x_s^2-1)} \left[ 2\mu r_s \cos(\phi)^2 x_s^2 \sqrt{1-x_s^2} + x_s^2 - 1 \right]
\] |
| 4     | \[
\frac{\mu r_s x_s \cos(\phi)}{360(x_s^2-1)} \left[ 8(\mu r_s)^3 x_s^6 \cos(\phi)^4 + 40\mu r_s x_s^4 \cos(\phi)^4 \right. \\
\left. -14\mu r_s x_s^4 + 32(\mu r_s)^2 x_s^4 \cos(\phi)^4 (1-x_s^2)^{1/2} \right. \\
\left. -8(\mu r_s)^3 x_s^4 \cos(\phi)^4 \right. \\
\left. -32(\mu r_s)^2 x_s^4 \cos(\phi)^2 (1-x_s^2)^{1/2} \right. \\
\left. +44\mu r_s x_s^4 \cos(\phi)^2 - 11(1-x_s^2)^{1/2} x_s^2 \right. \\
\left. -4x^2 \cos(\phi)^2 (1-x_s^2)^{1/2} - 44\mu r_s x_s^2 \cos(\phi)^2 \right. \\
\left. +32(\mu r_s)^2 x_s^2 \cos(\phi)^2 (1-x_s^2)^{1/2} \right. \\
\left. +11(1-x_s^2)^{1/2} - 14\mu r_s + 28\mu r_s x_s^2 \right]
\] |
| 5     | \[
\frac{\mu r_s x_s \cos(\phi)}{360(x_s^2-1)} \left[ 8(\mu r_s)^3 x_s^4 \cos(\phi)^4 (1-x_s^2)^{1/2} \right. \\
\left. +16(\mu r_s)^2 x_s^4 - 40(\mu r_s)^2 x_s^4 \cos(\phi)^4 \right. \\
\left. +8(\mu r_s)^3 x_s^4 \cos(\phi)^2 (1-x_s^2)^{1/2} \right. \\
\left. +24(\mu r_s)^2 x_s^4 \cos(\phi)^2 + 3x_s^2 \right. \\
\left. -6\mu r_s x_s^2 (1-x_s^2)^{1/2} - 3 + 16(\mu r_s)^2 \right. \\
\left. -8(\mu r_s)^3 x_s^2 \cos(\phi)^2 (1-x_s^2)^{1/2} \right. \\
\left. +6\mu r_s (1-x_s^2)^{1/2} - 32(\mu r_s)^2 x_s^2 \right. \\
\left. +36\mu r_s x_s^2 \cos(\phi)^2 (1-x_s^2)^{1/2} \right. \\
\left. -24(\mu r_s)^2 x_s^2 \cos(\phi)^2 \right]
\] |
3.1.4 Secondary Scattering for Off-Central Axis Beam

In this section, a numerical solution for the secondary scattering geometry, as illustrated in Fig. 3.5, is presented.

![Figure 3.5: The geometry of a secondary diffraction cone intersecting a spherical sample.](image)

The bounds of integration for the secondary scattering integrals are defined by the two illuminated volumes, i.e. of the principal beam and primary diffraction cones (refer to Fig. 3.3). For the principal beam this volume is given by

$$
\int_{0}^{r_{B}} \int_{0}^{2\pi} \int_{-\sqrt{r_{s}^2 - \rho^2}}^{\sqrt{r_{s}^2 - \rho^2}} dr_0.
$$

The volume of the primary diffraction cone originating from the point \((r_{0}, \rho, \xi)\) is obtained by an integral over \(2\theta_{1}, \phi_{1}\) and the path length from the diffracting volume to the edge of...
the sphere,
\[ \int_0^\pi \sin(2\theta_1) d2\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{R(r_0, 2\theta_1, \phi_1, \rho, \xi)} r_1^2 dr_1. \]  
(3.21)

The two-volume integral, for secondary scattering in an arbitrary spherical geometry is described by

\[ I_2(2\theta, \phi) = \left( I_0 n^2 \sigma_e^2 / r^2 \right) \int_0^{r_B} r ' dr ' \int_0^{2\pi} d\phi ' \int_0^{\sqrt{r_s^2 - r'^2}} dr_0 \times \int_0^\pi \sin(2\theta_1) d2\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{R(r_0, 2\theta_1, \phi_1, \rho, \xi)} dr_1 \times \exp \left[ -\mu r_0 - \mu r_1 - \mu \sqrt{r_s^2 - r'^2} - \mu R(z_1, 2\theta, \phi_1, \rho_1, \xi_1) \right] \times P(\kappa_0, 2\theta_1, \phi_1) J(2\theta_1) P(\kappa_1, 2\theta_2, \phi_2) J(2\theta_2). \]  
(3.22)

The path length from the secondary scattering volume to the surface of the sphere is \( R(z_1, 2\theta, \phi, \rho_1, \xi_1) \), where \((z_1, \rho_1, \xi_1)\) is the point of secondary scattering in cylindrical coordinates. The values of \(z_1, \rho_1\) and \(\xi_1\) are defined by \(z_1 = r_0 + r_1 \cos (2\theta_1)\),

\[ \xi_1 = \tan^{-1} \left\{ \frac{r ' \sin(\phi ') + r_1 \sin(2\theta_1) \sin(\phi_1)}{r ' \cos(\phi ') + x + r_1 \sin(2\theta_1) \cos(\phi_1)} \right\} - \pi \]

and

\[ \rho_1 = \left\{ \left[ r ' \cos(\phi ') + x + r_1 \sin(2\theta_1) \cos(\phi_1) \right]^2 \right. \]

\[ + \left. \left[ r ' \sin(\phi ') + r_1 \sin(2\theta_1) \sin(\phi_1) \right]^2 \right\}^{1/2}. \]

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As with the spherical absorption correction, the number of parameters can be reduced by scaling to $r_s$, yielding

$$I_2 (2\theta, \phi) = \left( I_0 r_s^4 n^2 \sigma_e^2 / r^2 \right) \int_{r_s}^{r_B s} r' dr' \int_0^{2\pi} d\phi' \int_{-\sqrt{1-\rho_s^2}}^{\sqrt{1-\rho_s^2}} dr_0 s $$

$$\times \int_0^\pi \sin(2\theta_1) d2\theta_1 \int_0^{2\pi} d\phi_1 \int_{0}^{r_s} R_s (r_0 s, 2\theta_1, \phi_1, \rho_1 s, \xi) dr_1 s$$

$$\times \exp \left[ -\mu r_s r_0 s - \mu r_s r_1 s - \mu r_s \sqrt{1 - \rho_s^2} \right.$$

$$-\mu r_s R_s (z_{1s}, 2\theta, \phi, \rho_{1s}, \xi_1) \bigg]$$

$$\times P (\kappa_0, 2\theta_1, \phi_1) J (2\theta_1) P (\kappa_1, 2\theta_2, \phi_2) J (2\theta_2) \bigg].$$

The evaluation of Eq. 3.23 is made more difficult by the finite size of the beam. In the small beam limit, however, two of the six integrals become trivial and $\rho \to x$ such that Eq. 3.22 reduces to

$$I_2 (2\theta, \phi) = \left( I_0 \pi r_B^2 r_s^2 n^2 \sigma_e^2 / r^2 \right) \int_{-\sqrt{1-x_s^2}}^{\sqrt{1-x_s^2}} dr_0 s$$

$$\times \int_0^\pi \sin(2\theta_1) d2\theta_1 \int_0^{2\pi} d\phi_1 \int_{0}^{r_s} R_s (r_0 s, 2\theta_1, \phi_1, x_s, \xi) dr_1 s$$

$$\times \exp \left[ -\mu r_s r_0 s - \mu r_s r_1 s - \mu r_s \sqrt{1 - x_s^2} \right.$$

$$-\mu r_s R_s (z_{1s}, 2\theta, \phi, \rho_{1s}, \xi_1) \bigg]$$

$$\times P (\kappa_0, 2\theta_1, \phi_1) J (2\theta_1) P (\kappa_1, 2\theta_2, \phi_2) J (2\theta_2) \bigg].$$
Since the corrected intensity is described by Eq. 3.4, the ratio of secondary scattering intensity to primary scattering intensity is given by

\[ I_2(2\theta, \phi) / I_1(2\theta, \phi) = \left\{ r_s n \sigma_e V / \left[ 2P(\kappa_0, 2\theta, \phi) J(2\theta) V' \right] \right\} \int_{-\sqrt{1-x_s^2}}^{\sqrt{1-x_s^2}} dr_{0s} \]

\[ \times \int_0^\pi \sin(2\theta_1) d2\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{R_s(r_{0s,2\theta_1,\phi_1,x_1})} dr_{1s} \]

\[ \times \exp \left[ -\mu r_s r_{0s} - \mu r_s r_{1s} - \mu r_s \sqrt{1 - x_s^2} \right. \]

\[ -\mu r_s R_s \left( z_{1s}, 2\theta, \phi, \rho_{1s}, \xi_1 \right) \]

\[ \times P(\kappa_0, 2\theta_1, \phi_1) J(2\theta_1) P(\kappa_1, 2\theta_2, \phi_2) J(2\theta_2). \]  

(3.25)

To convert this to the form of Eq. 3.12, the substitution \( r_s n \sigma_e = \sigma_e N_A \mu r_s / \sum \chi_i M_i (\mu/\rho)_i \) is made so that \( Q_M \) for offset spherical geometry is given by

\[ Q_M = \left\{ N_A \sigma_e \mu r_s V / \left[ 2P(\kappa_0, 2\theta, \phi) V' \right] \right\} \int_{-\sqrt{1-x_s^2}}^{\sqrt{1-x_s^2}} dr_{0s} \]

\[ \times \int_0^\pi \sin(2\theta_1) d2\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{R_s(r_{0s,2\theta_1,\phi_1,x_1})} dr_{1s} \]

\[ \times \exp \left[ -\mu r_s r_{0s} - \mu r_s r_{1s} - \mu r_s \sqrt{1 - x_s^2} \right. \]

\[ -\mu r_s R_s \left( z_{1s}, 2\theta, \phi, \rho_{1s}, \xi_1 \right) \]

\[ \times P(\kappa_0, 2\theta_1, \phi_1) J(2\theta_1) P(\kappa_1, 2\theta_2, \phi_2) J(2\theta_2) / \left( \sum \chi_i Z_i^2 \right)^2. \]  

(3.26)

The large number of parameters makes the tabulation of \( Q_M \) difficult. Instead, it can be obtained from a numerical integration, given values of \( \kappa_0, x_s, \mu r_s, 2\theta, \phi \) and \( J(2\theta) / \left( \sum \chi_i Z_i^2 \right) \).
Since $J(2\theta)$ is unknown, the computation of $Q_M$, which is independent of the experimental data, may be obtained if $J(2\theta)$ is approximated by $\sum \chi_i [f_i^2 + i(M)_i]$ [10–12]. Unlike for standard transmission and reflection geometries, the analytic approximation for $J(2\theta)/(\sum \chi_i Z_i^2) = q + \{(1 - q)/(1 + b\sin^2(\theta))\}$ [10–12] provides little benefit here. The approximation for $J(2\theta)$ as the average atomic scattering intensity diverges strongly from the true values of $J(2\theta)$ at small angles and, therefore, may not be appropriate for small angle data with large $\mu r_s$. Following Malet, Cabos and Delord [19], the experimental $I(2\theta)$, after removing polarization and absorption effects and scaling to electron units, is used as an approximate form of $J(2\theta)$ in the secondary scattering integral. Practically, the experimental $I(2\theta)$ is limited to some $2\theta_{\text{Max}}$ after which the $[\sum \chi_i (f_i^2 + i(M)_i)]$ approximation is appropriate. The suggested approximation for $J(2\theta)$ is shown in Eq. 3.27 where the normalization constant $N$ is chosen to match the two approximate forms of $J(2\theta)$ at $2\theta_{\text{Max}}$.

$$J(2\theta) \approx \begin{cases} \frac{1}{N} \frac{1}{2\pi} \int_0^{2\pi} d\phi \frac{I(\phi, 2\theta)V}{P(\kappa_0, 2\theta, \phi)V'} & \text{for } 2\theta \leq 2\theta_{\text{Max}} \\ \left(\sum \chi_i (f_i^2 + i(M)_i)\right) & \text{for } 2\theta \geq 2\theta_{\text{Max}} \end{cases}$$ (3.27)

In principle, the calculation of $I_2/I_1$ can be iterated with successively better approximations for $J(2\theta)$; however, this is too computationally intensive to be practical.

### 3.1.5 Results and Discussion

Three special cases of the integral forms of absorption and secondary scattering derived in the previous section for an X-ray beam incident on a spherical amorphous sample are of particular interest. The first is the case of a non-polarized beam incident on the center of the sample ($x_s = 0, \kappa_0 = 0$). For the second case, where the incident beam is off to one side of
the central axis, the asymmetry in the measured intensity is greatest for strongly absorbing
samples. To illustrate this, we chose \( x_s > 0 \) and \( 2\mu r_s = 10 \). For the third, the average
corrections about the azimuthal angle are evaluated, indicating that there remains a strong
dependence of the correction to the degree of off-axis transmission after angular averaging.
Unless otherwise noted synchrotron wavelengths \((\approx 0.1 \text{ Å})\) were used for calculations of
\( I_2/I_1 \).

The first case is unique; both the absorption and secondary scattering corrections are sym-
metric in \( \phi \) so that they can be applied directly to the one-dimensional \( I(q) \) data, obtained
by a circular average of the detector intensity as a function of \( q \). The calculated spherical
absorption corrections normalized to \( \exp(-2\mu r_s) \) for \( 2\mu r_s = 0.1, 1 \) and 10 are shown in Fig.
3.6.a. The secondary scattering corrections for the same \( \mu r_s \) are also shown, Fig. 3.6.b. For
these calculations, the \( J(2\theta)s \) were taken to have the form of the atomic scattering factor
for Si, Zr and Au. These elements have the appropriate densities and linear absorption
coefficients at synchrotron wavelengths to attain these values of \( \mu r_s \) for samples sizes that
are appropriate for the beamline ESL [1]. The absorption corrections shown in Fig. 3.6
were computed numerically, although a fifth order asymptotic expansion, Eq. 3.19, agrees
to within 2% at \( 2\theta = 30^\circ \) for \( 2\mu r_s = 10 \), and is indistinguishable from the numerical solution
for \( 2\mu r_s = 1 \). The secondary scattering also depends on wavelength through \( J(2\theta) \), as shown
in Fig. 3.6.c: higher energy (\( i.e. \) lower wavelength) results in a more rapid increase of \( I_2/I_1 \)
with momentum transfer and diffraction angle (not shown).

Off-central-axis alignment, the second case, results in a dramatically asymmetric detector
intensity pattern, requiring a two-dimensional correction. Figures 3.7.a - 3.7.d show the
absorption correction for the intensity measured with an area detector for \( 2\mu r_s = 10 \) for
\( x_s = 0, 0.1, 0.3 \) and 0.5 respectively. The absorption correction as a function of scattering
Figure 3.6: Dependence of the absorption correction (a) and secondary scattering intensity on attenuation (b) and energy (c) in centered spherical geometry.

angle, $2\theta$, for the $\phi = 0$ axis, using the same values of $2\mu r_s$, is shown in Fig. 3.7.e. The secondary scattering intensities, assuming values for Au, $\kappa_0 = 0$, $2\mu r_s = 10$, and $x_s=0$, 0.1, 0.3 and 0.5, are shown in Figs. 3.8.a – 3.8.d. The ratios of secondary to primary scattering
intensities as a function of $2\theta$, for $\phi = 0$, are shown in Fig. 3.8.e. The asymmetry observed in the measured intensity due to the incidence of the X-ray beam off-incidence with the axis through the center of the sample is dominated by absorption corrections. However, a corresponding asymmetry in the secondary scattering correction is also found.

Figure 3.7: Simulated two-dimensional detector image asymmetry in the absorption correction normalized to the beam center for $2\mu r_s = 10$ caused by off-axis beam incidence at (a) $x_s = 0$, (b) $x_s = 0.1$, (c) $x_s = 0.3$ and (d) $x_s = 0.5$, and (e) along the $x$-axis ($\phi = 0$).
Since the integral average around the azimuthal angle is often taken for symmetric area detectors, the effect of misalignment on the angular averaged corrections is considered. As shown in Fig. 3.9 for Au, $2\mu r_s = 10$ and $x_s = 0, 0.1, 0.3, 0.5$ and 0.8, curvature of the averaged absorption correction changes dramatically with increasing $x_s$, from negative
curvature at near-central-axis alignment to positive curvature as the degree of misalignment increases. Also shown in Fig. 3.9, the angular averaged secondary scattering intensity systematically decreases with increasing $x_s$. From perturbations of $2\mu r_s$ and $\lambda$ about the Zr, $2\mu r_s = 1$, $\lambda = 0.1$ case, the parameter space in which the angular average corrections remains within 1% of the centrally aligned beam case ($x_s = 0$) at $2\theta = 30^\circ$ is bound by $x_s < 0.45 - 0.2 \ln (2\mu r_s) + 3.2 \AA^{-1} (\lambda - 0.1\AA)$. Within this region of parameter space the centrally aligned beam may be used as an approximation of the offset spherical absorption correction.

Figure 3.9: Azimuthal averaged absorption correction (upper) and secondary scattering intensity (lower) in with off-central-axis alignment.
In situations where the sample cannot be accurately aligned using a transmission measurement, the degree and angle of off-central-axis alignment (i.e. $x_s$ and $\xi_0$) may be unknown. Since liquids are isotropic, $J(2\theta)$ should be axially symmetric, so these parameters can be solved using the observed detector asymmetry. For an area detector that is perpendicular, or tilt corrected, to the transmitted X-ray beam and has been background and gain corrected, any asymmetry present in the detected scattering intensity from the amorphous samples can be attributed to polarization effects and an X-ray beam that is displaced from the central axis of the sample. The polarization effects are described by Eq. 3.2. After making the polarization correction, the azimuthal angle of maximum intensity at constant $2\theta$ identifies the angle of the offset in Fig. 3.3, $(\xi_0 + \pi)$. A non-linear fitting approach may then be used to determine the value of $x_s$ that removes the asymmetry from the detector image.

### 3.1.6 Concluding Remarks

Corrections to improve the analysis of scattering data studies from liquids are critically important. The artifacts arising from an improper alignment of the sample, such as asymmetric absorption and secondary scattering intensity, can produce poor data that cannot be analyzed quantitatively. This section presents the development of corrections for absorption and secondary scattering intensity when a partially polarized X-ray beam of size smaller than the size of a liquid sample processed in a containerless environment is incident upon the sample, but displaced from the central axis. While the corrections obtained are expressed in integral form, current computing resources allow rapid evaluations for any given set of parameters.
3.2 Pair Distribution Function Analysis of X-ray Diffraction from Amorphous Spheres in an Asymmetric Transmission Geometry: Application to a Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ Glass [3]

3.2.1 Introduction

The first pair distribution function (PDF) analysis of liquid diffraction data was demonstrated for liquid mercury in 1930 [20], seventeen years after the first X-ray interference measurements of non-crystalline materials [21]. Since then the PDF method has been used in complex materials as a quantitative tool for comparing experimental X-ray and neutron data with predictions from theoretical models [22]. For liquids and other amorphous materials modeling approaches such as Reverse Monte Carlo and Molecular Dynamics simulations are being used to obtain increasingly more comprehensive structural information from the measured PDFs [23–25]. For these modeling efforts to succeed the experimental data must not only be of the highest possible quality, but methods for quantitatively estimating the error must be addressed.

There is an increasing interest in structural studies of high-temperature metallic liquids and the glasses that they form. While amorphous ribbons or in some cases ingots of metallic glasses can be studied, currently the best method for acquiring high quality diffraction data from metallic liquids in their supercooled state (i.e. below the equilibrium melting temperature) is with levitation techniques. These techniques allow liquids to be processed in
an inert, contactless, environment and remove one of the major sources of heterogeneous nucleation (*i.e.* the container), allowing supercooling to be extended. Electrostatic levitation, electromagnetic levitation, and aerodynamic levitation have been used for laboratory X-ray, synchrotron, and/or neutron scattering studies of supercooled liquids [1,4–9]. In many cases, however, proper corrections have not been made to obtain the final data. Absorption corrections are often based on geometries different from the spherical samples studied, and the effect of off-axis incident radiation is generally not considered. Here, experimental synchrotron scattering data from a spherical Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ (Vitreloy 106a) glass will be used to motivate a discussion of the corrections relevant for beamline experiments on amorphous samples and to verify the methods proposed. Particular attention is focused on the recently-reported semi-analytic correction for small beam secondary scattering within and absorption through an off-axis aligned spherical sample (Sect. 3.1) [2]. The propagation of uncertainties from these corrections, sampling statistics, and structure function termination to the PDFs obtained are also discussed.

### 3.2.2 Experiment

Ingots (≈ 1.0 g) of Vitreloy 106a were prepared by arc-melting high-purity elemental Zr (99.95%), Cu (99.999%), Ni (99.995%), Al (99.999%) and Nb (99.95%) on a water-cooled copper hearth in a Ti-Zr gettered high-purity Ar (99.999%) atmosphere. For density measurements a 4 mm by 2 mm by 15 mm amorphous bar was prepared by suction casting an ingot under the same arc-melting conditions. For X-ray diffraction measurements a small approximately spherical sample with a mass of 72.5 mg (2.74 mm diameter) was formed by re-melting under the same conditions a portion of a crushed ingot. As mentioned, this sample was used to mimic liquid samples used for high-energy X-ray diffraction measurements.
in the beamline electrostatic levitation technique [1]. Due to the ease of glass formability for Vitreloy 106a, the re-melted sphere and cast bar were amorphous, confirmed by the X-ray diffraction measurements.

Density measurement of the glass bar was made using the Archimedean technique with a Cahn C-29 precision electro-balance, having a precision of ± 5 µg. The sample bar was weighed at room temperature (20 °C) in air, which has a density of 0.0012 g cm\(^{-3}\) [26], and in toluene, which has a density of 0.8674 g cm\(^{-3}\) [27]. The density of the glass sample is \(\rho_s = (\rho_{\text{Air}}w_{\text{Toluene}} - \rho_{\text{Toluene}}w_{\text{Air}})/(w_{\text{Air}} - w_{\text{Toluene}})\), where \(\rho\) and \(w\) are the density and measured weight respectively. The measured density of Vitreloy 106a was 6.7158 ± 0.0075 g cm\(^{-3}\).

X-ray diffraction measurements were performed at the Advanced Photon Source (Station 6-ID-D in the MUCAT Sector) using a monochrome beam with an energy of 99.8 keV and a 0.35 mm by 0.35 mm profile. Diffraction data were obtained in air in a transmission geometry using a GE Revolution 41-RT amorphous Si flat-panel X-ray detector with 200 µm by 200 µm pixels, located approximately 200 mm beyond the sample. Measurements were acquired over a \(q\)-range from 1 Å\(^{-1}\) to 17 Å\(^{-1}\), where \(q\) is the momentum transfer \(q = 4\pi\sin(\theta)/\lambda\). The spherical Vitreloy 106a sample was placed between Kapton\(^{\text{TM}}\) tape and mounted on a Huber six-circle goniometer to provide accurate positioning. To test the spherical corrections, diffraction images were acquired at five positions, separated by 0.5 mm vertical steps, beginning at 0.5 mm from the bottom of the sample to the top (Fig. 3.10).

The X-ray absorption by the sample at each position was determined from the measured photocurrents in a biased photodiode located on the X-ray incident and exit sides of the sample. The ratio of transmitted intensity to incident intensity is related to the attenuation coefficient, \(\mu\), according to Beer’s law \(I_{\text{Transmitted}}/I_{\text{Incident}} = \exp(-\mu t)\), where \(t\) is the sample
thickness at each position, $I_{\text{Transmitted}}$ is the measured photocurrent for the transmitted X-ray flux through the sample, and $I_{\text{Incident}}$ is the photocurrent for the incident beam. This ratio was measured at each sample position. By assuming a circular cross section and $\mu/\rho = 0.83$ for the Vitreloy 106a sample [28], the coordinates of each measurement position relative to the sample center were determined by a least-squares minimization of the difference between the measured $\mu t$ and the expected $\mu t$. The resulting fit indicated that the measured positions (numbered 1-5 starting from the sample bottom in Fig. 3.10) began 0.27 mm horizontally and 0.84 mm below the sample center. This was consistent with the best fits of the asymmetry in the X-ray images to that predicted by the self-absorption correction, as will be described later.

### 3.2.3 X-ray Analysis

A number of corrections are required to convert the measured intensity data from the image plate detector to the structure function (often called the structure factor in liquid and glass
communities), \( S(q) \). Although several X-ray data analysis software packages for this are available [29–31], the assumptions used in these packages are not always transparent to the user. Further, no existing software packages incorporate corrections for spherical samples. An in-house software package operating in LabVIEW\textsuperscript{TM} (\textit{X-ray Batch.vi}, see Appendix C) was developed to include these corrections when calculating the structure and pair distribution functions for diffraction data obtained for such samples in transmission mode, with the geometry shown in Fig. 3.11.

![Figure 3.11: Diffraction data obtained in the transmission mode with an image detector for spherical samples.](image)

### 3.2.3.1 Background and Gain Corrections

It is important to account for the interaction of the incident X-ray beam with the sample container and for dark signals in the detector, since these can be of the order or greater than the intensity obtained from weakly scattering amorphous samples. To do this, the intensity measured by the image detector when the X-ray beam is incident on an empty experimental chamber, \( I_{\text{Background}} \), is subtracted from the scattered intensity from the sample, \( I_{\text{Sample}} \).
account for the variable efficiency of each pixel in the area detector, a multiplicative factor (i.e. a gain map $\Gamma$) must also be included, giving

$$I_{Corrected}(R, \phi') = \Gamma(R, \phi') \left[ I_{Sample}(R, \phi') - I_{Background}(R, \phi') \right].$$

(3.28)

As indicated, the gain map is a function of the detector coordinates $(R, \phi')$. It is empirical, generally energy dependent, and is unique to each detector. It is usually supplied by the detector manufacturer, but since it is energy dependent it is important to make sure that this corresponds to the energy range used in the scattering experiment.

### 3.2.3.2 Tilt Corrections

While the schematic illustration of the scattering and detector geometry shown in Fig. 3.11 places the detector perpendicular the scattering cone, realistically it is generally impractical or impossible to precisely align a flat plate detector. For an arbitrary detector orientation (Fig. 3.12), the detector polar coordinates $(R, \phi')$ can be mapped to solid angle coordinates $(2\theta, \phi)$, by knowing the angle and magnitude of maximum tilt toward the sample, $\phi_0$ and $\tau_0$ respectively. For the studies discussed here, these were measured using diffraction rings from a silicon standard, although other standards with well-known d-values are often used as well (e.g. sodium chloride and cerium dioxide). Around the polar angle of diffraction, $\phi$, the angle-dependent tilt along a radial profile of the detector face, $\tau(\phi)$, is given by

$$\tan[\tau(\phi)] = \tan(\tau_0) \cos(\phi - \phi_0).$$

(3.29)
Figure 3.12: Schematic representation of diffraction data obtained in the transmission mode with a tilted image detector.

The angular tilt and the distance from the sample to the detector at beam center (\textit{i.e.} the working distance), $D$, fixes the relationship between $R$ and $2\theta$, as described by

$$ R = \frac{D \sin(2\theta)}{\cos[2\theta - \tau(\phi)]}. \quad (3.30) $$

The tilt also transforms the polar angles between coordinate systems by

$$ \tan(\phi' - \phi_0') = \tan(\phi - \phi_0) \cos(\tau_0). \quad (3.31) $$

Though presented in polar coordinates, these equations are equivalent to those reported by Hammersley [29]. To avoid confusion the explicit dependence of the tilt on polar angle is dropped for the remainder of this review (\textit{i.e.} $\tau(\phi) \rightarrow \tau$).
3.2.3.3 Geometric Correction

The transform from detector coordinates to solid angle coordinates also requires a conversion of the intensity measured at a given pixel. The intensity measured at the detector coordinate is a factor of \(d\Omega/dA\) smaller than the intensity at the corresponding solid angle coordinate,

\[
\frac{d\Omega}{dA} = \frac{\sin(2\theta) \partial 2\theta \partial \phi}{R \partial R \partial \phi'} = \frac{\cos^3(2\theta - \tau) \cos(\tau_0)}{\cos^3(\tau) D^2}.
\]

The conversion to solid angle flux (normalized to the beam center) is obtained by multiplying the intensity for the corresponding pixel on the flat plate detector by \(\cos^3(\tau) \cos^{-3}(2\theta - \tau)\).

3.2.3.4 Oblique Incidence

The oblique incidence correction for plane detectors takes account of the additional distance that a diffracted photon travels in the detector, compared with that for normal incidence. This additional distance within the detector’s active region increases the detector efficiency at high angles. The additional distance for an oblique incident beam is \(t_0/\cos(2\theta - \tau)\), where \(t_0\) the perpendicular thickness. The additional multiplicative gain, \(O\), associated with the increased distance is

\[
O = \frac{1 - T_{\perp}^{1/\cos(2\theta - \tau)}}{1 - T_{\perp}},
\]

where \(T_{\perp}\) is the transmission of the X-rays through the detector for normal incidence [32]. In the GE A-Si detector used in this study, the X-rays cause fluorescence in an approximately 500 µm thick CsI layer that is deposited on A-Si [33]. Based on the linear attenuation of CsI, for 0.13 MeV photons, \(T_{\perp}\) was set at 0.75 for these measurements [28].
3.2.3.5 Polarization Correction

Radiation polarized in the scattering plane is attenuated by a factor of $\cos(2\theta)^2$, while radiation polarized perpendicular to the scattering plane is not attenuated. The polarization of the X-rays that are incident on the sample is given by $\kappa = (I_{0x} - I_{0y}) / (I_{0x} + I_{0y})$, where $I_{0x}$ and $I_{0y}$ are the intensities of the incident beam polarized in the $\phi = 0$ and $\phi = \pi/2$ planes respectively. The attenuation of the resulting diffraction pattern is given by [17,18]

$$P(\kappa, 2\theta, \phi) = 1/2 + \kappa \left[ \sin^2 (\phi) - \cos^2 (\phi) \right] / 2$$
$$+ \left\{ 1 + \kappa \left[ \cos^2 (\phi) - \sin^2 (\phi) \right] \right\} \cos^2 (2\theta)/2. \tag{3.34}$$

The intensity from each pixel in the detector is divided by this factor to correct for scattering into different polarization states, and to ultimately generate the correct scattering cross section.

3.2.3.6 Self-Absorption and Secondary Scattering Corrections

Self-absorption accounts for the attenuation within the sample of the scattered X-rays. Secondary scattering occurs when the diffracted beam is again scattered before exiting the sample. The absorption and secondary scattering factors were derived recently for spherical samples, though not experimentally verified (see Sect. 3.1) [2]. For the case where the X-rays are incident on a spherical sample at a position that is above or below the sample center,
the self-absorption correction is a two-dimensional multiplicative factor given by

\[
\frac{V}{V'} \sim \exp \left( \frac{2 \mu_r s \sqrt{1 - x_s^2}}{\sqrt{1 - x_s^2}} \right) \sum_{i=0}^{\infty} A_i (\mu_r s, x_s, \phi) (2\theta)^i,
\]

\(2\theta \to 0, r_{B_s} = 0,
\]

where \(r_s\) is the sample radius, \(r_{B_s}\) is the beam radius scaled to sample radius, \(x_s\) is the fraction of off-axis beam alignment (i.e. 0 centered 1 at the sample edge) and \(A_i\) are the coefficients of the small angle expansion, which are specified in Table 3.2. The secondary scattering factor is the ratio of the secondary to primary scattering

\[
\frac{I_2}{I_1} (2\theta, \phi) = \frac{(\sum \chi_i Z_i^2)^2 Q_M}{J(2\theta) \sum \chi_i M_i (\mu/\rho)_i},
\]

where \(Q_m\) is a geometry dependent integral [10]. For a spherical sample with off-axis transmission by a small X-ray beam, it can be shown that the \(Q_m\) is described by

\[
Q_M = \left\{ N_A \sigma_s \mu_r s V / \left[ 2P(\kappa_0, 2\theta, \phi) V' \right] \right\} \int_{-\sqrt{1-x_s^2}}^{\sqrt{1-x_s^2}} dr_{0s} \\
\times \int_0^{\pi} \sin(2\theta_1) d2\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} R_s (r_{0s}, 2\theta_1, \phi_1, x, \xi)  \\
\times \exp \left[ -\mu_r s r_{0s} - \mu_r s r_{1s} - \mu_r s \sqrt{1 - x_s^2} \\
- \mu_r s R_s (z_{1s}, 2\theta, \phi, \rho_{1s}, \xi_1) \right] \\
\times P(\kappa_0, 2\theta_1, \phi_1) J(2\theta_1) \\
\times P(\kappa_1, 2\theta_2, \phi_2) J(2\theta_2) / \left( \sum \chi_i Z_i^2 \right)^2.
\]

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A more detailed discussion of the notation used here and the results of an integration of Eq. (3.37) can be found in Sect. 3.1.

3.2.3.7 Angular Average

Isotropic and homogenous samples having no preferred directionality, such as liquids, produce diffraction patterns that are symmetric about the polar coordinate. To take advantage of this symmetry and to reduce noise in the measurement, the intensities of the pixels located at a given $2\theta$ from the beam center are averaged about the polar angle to give a one-dimensional diffraction pattern [29].

3.2.3.8 Compton Scattering

The Compton scattering, $n^{Inc}(q)$, which is subtracted from the measured intensity per atom, is given by $(E_C/E)^{\alpha}$ $i(M)$, where $(E_C/E)^{\alpha}$ is the Breit-Dirac recoil factor and $i(M)$ is the intensity of modified scattering, defined by

$$i(M) = \sum \chi_i Z_i - \sum \chi_i \left( \sum f_e^2 \right) .$$

(3.38)

In Eq. (3.38) $\chi_i$ is the atom fraction of element $i$, $Z_i$ is the atomic number of element $i$ and $\sum f_e^2$ is the sum over the square of the electron form factors [34]. Analytical fits to $\sum f_e^2$ were published by Balyuzi in 1975 for $Z = 0$ to 95 and are good for $0 < q < 17.59$ (Å$^{-1}$) [35].

The Breit-Dirac recoil factor is a small multiplicative correction to the theoretical Compton profile that accounts for radiation pressure on a scattering element. The energy dependence
of Compton scattering is given by the Klein-Nishina formula,

\[ \frac{E_C}{E_0} = \frac{1}{1 + \frac{2E_0}{m_ec^2}\sin^2(\theta)}, \]  

(3.39)

where \( E_0 \) is the incident photon energy. The energy dependence is scaled by the exponent, \( \alpha \), which has a value of three for intensity measuring detectors (as in this study) and two for counting detectors [36].

3.2.3.9 Fluorescence

Fluorescence, \( F \), occurs when the atoms absorb the incident photons and reemit at a longer wavelength. This creates a uniform background over all solid angles. In general, the magnitude of the fluorescence scales with the atomic number of the constituent elements of the sample. However, a precise value for this background is usually unknown, because the energy dependence of the detector is usually not known and because the absorption and reemission properties are difficult to predict from sample to sample. Due to these uncertainties, fluorescence is determined in conjunction with the intensity normalization through fitting. When the fluorescence values obtained are unphysical, the fitting parameter takes on the role of an arbitrary scaling proposed by Peterson [37]. Since the Vitreloy 106a glass in this work contains no fluorescing elements near the energy used, and an additional fitting parameter is found to be not necessary for high quality analysis, no fluorescence correction is applied in these studies.
3.2.3.10 Intensity Normalization

The intensity normalization, \( N \), scales the intensity from arbitrary detector units to electron units. The conversion factor is found by a minimization of the Peterson metric [37], defined by

\[
\Delta G_{\text{low}} = \frac{\int_0^{r_{\text{low}}} \left[ rG(r) - \frac{r^2}{r_{\text{low}}} \int_0^{r_{\text{low}}} rG(r)dr \right]^2 dr}{\int_0^{r_{\text{low}}} \left[ \frac{r^2}{r_{\text{low}}} \int_0^{r_{\text{low}}} rG(r)dr \right]^2 dr},
\]

(3.40)

where \( G(r) \) is the reduced pair distribution function (or RPDF) and \( r_{\text{low}} \) is the hard sphere cut-off, where the probability of find an atom a distant \( r < r_{\text{low}} \) is 0. The Peterson metric quantifies unphysical ripples in \( G(r) \) within the hard sphere limit. It is assumed that the correct normalization will result in the most physical low-\( r \) behavior in \( G(r) \). To remove user variability \( r_{\text{low}} \) is set by the experimental data as \( 3\pi/2q_{\text{FirstPeak}} \), where \( q_{\text{FirstPeak}} \) is the location of the first peak in the diffraction pattern.

3.2.3.11 Coherent Scattering Cross-section and Structure Function

When all corrections are applied, the conversion of the intensity measurements from the detector intensity to the coherent scattering cross section \( d\sigma_C/d\Omega \) is calculated by

\[
\frac{d\sigma_C}{d\Omega} = N \int d\phi \left\{ \frac{(V/V')}O^{-1}P^{-1} (1 + I_2/I_1)^{-1} (dA/d\Omega) \times \left[ \Gamma(R, \phi') (I_{\text{Raw}}(R, \phi') - I_{\text{Background}}(R, \phi')) \to (2\theta, \phi)]/2\pi \right\} - n^{\text{Inc}} - F \right\}
\]

(3.41)

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where the notation $[F(R, \phi') \rightarrow (2\theta, \phi)]$ indicates a change of variable from $(R, \phi')$ to $(2\theta, \phi)$ and $\int d\phi [F(2\theta, \phi) / 2\pi]$ denotes an average about the coordinate $\phi$.

The structure function $S(q)$ is a scaled form of the coherent scattering cross-section to remove the monotonic cross-section [Laue diffuse scattering $\sum \chi_i f_i^2 - (\sum \chi_i f_i)^2$] and to normalize the intensity by the square average atomic form factor,

$$ S(q) = \frac{(d\sigma_C/d\Omega)}{(\sum \chi_i f_i)^2} \left[ (\sum \chi_i f_i^2) - (\sum \chi_i f_i)^2 \right] / (\sum \chi_i f_i)^2. $$  \hspace{1cm} (3.42)

The atomic form factor of the $i^{th}$ atom, $f_i$ is calculated from analytic fits to X-ray form factors reported by Waasmaier and Kirfel for $0 < q < 75.40\ \text{Å}^{-1}$ [38].

### 3.2.3.12 Reduced Pair Distribution Function and Pair Distribution Function

The reduced pair-distribution function (RPDF) is the Fourier transform of the structure function

$$ G(r) = \frac{2}{\pi} \int_0^\infty q [S(q) - 1] \sin(qr) dq. $$  \hspace{1cm} (3.43)

Since the structure function is measured at discrete intervals over a finite experimental range, $q_{\text{min}}$ to $q_{\text{max}}$, the Fourier integral in Eq. (3.43) is truncated and computed using numerical methods. For a discrete $S(q)$ over the range $q_{\text{min}}$ to $q_{\text{max}}$, $G(r)$ is computed on a 0.01 Å spaced grid in $r$ by

$$ G(r) = \frac{1}{\pi} \sum_{i=0}^{N-1} \{ q_i [S(q_i) - 1] \sin(q_i r) $$

$$ + q_{i+1} [S(q_{i+1}) - 1] \sin(q_{i+1} r) \} (q_{i+1} - q_i). $$  \hspace{1cm} (3.44)
At high $q$, the structure function approaches unity and therefore will no longer contribute to the integral. At low $q$, the structure function approaches a small constant [39, 40]. To limit the impact of truncation error, the structure function from zero to $q_{\text{min}}$ is approximated as the lowest $q$ experimental measurement, $S(q_{\text{min}})$. Although it is common to smooth the RPDF, either by moving averages [36] or damping functions applied to $S(q)$ [41,42], the data reported here are the results of a direct Fourier transform without smoothing.

The pair distribution function (PDF), $g(r)$, is frequently reported instead of the RPDF because the interpretation of $g(r)$ is often more direct. As shown in Eq. (3.45), $g(r)$ is computed by normalizing $G(r)$ to the number density $\rho_0$ and scaling by $1/r$ to give the probability of finding a particle a distance $r$ from the average atom in the sample,

$$g(r) = \frac{G(r)}{(4\pi\rho_0 r)} + 1.$$  

(3.45)

### 3.2.3.13 Estimates of Uncertainty in the Structure Function

The experimental structure function is a discrete measurement in $q$, with statistical error at each measurement. The statistical error can be estimated by counting methods [43] or, as in this analysis, from the standard error of the intensity at a constant diffraction angle [29]. To accurately assess the statistical error this standard deviation must be performed during the angular average step in the analysis and after all two-dimensional corrections. Additional errors in the structure function arise from incorrectly applied corrections. Although these are difficult to quantify, the uncertainty in the structure function due to these errors can be estimated from the confidence intervals of the fit parameters, i.e. fluorescence and normalization.
3.2.3.14 Estimates of Uncertainty in the Real Space Correlation Functions

Uncertainties in the RPDF and PDF are rarely reported because correlations between data make error estimates difficult to obtain. From the Nyquist-Shannon theorem, the experimental structure is described by a RPDF calculated on a grid in \( r \) having a \( \pi/q_{\text{max}} \) spacing [22,36]. For a \( q_{\text{max}} = 17 \, \text{Å}^{-1} \), \( r_{\text{Nyquist}} = 0.18 \, \text{Å} \) which is an order of magnitude larger than the standard grid spacing of 0.01 Å [36]. Since no additional information is obtained when the RPDF is calculated on a finer grid, neither the reported data nor the reported error will be independent from the neighboring points. It has been argued that the RPDF should be reported on a Nyquist grid for this reason [22]. This may be misleading, however, since the oversampling is often justified by the physical constraint that the structure function must approach unity at high \( q \). If little structural information exists beyond the experimental \( q_{\text{max}} \), real features may be unobserved on a Nyquist grid but appear at the standard grid spacing. For this reason the RPDF and PDF are presented on an oversampled grid with the uncertainty at each point not shown.

Rather than reporting error propagation to the oversampled correlation functions, the error propagation to model fits are reported. For this analysis, a simple model was chosen to identify peaks in the PDF of amorphous Vitreloy 106a. The peaks are defined as the points where the derivative with respect to \( r \) is zero, determined numerically from the correlation function. The magnitude and position of the peaks are the parameters of the model. Uncertainties in these quantities were propagated by direct numerical methods.

For an arbitrary parameter \( Y \) the uncertainty in \( Y \) due to uncertainty in the variable \( X \) is described by \( \delta Y = |(\partial Y/\partial X) \delta X| \). Numerically this can be observed by changing the parameter \( X \) by its uncertainty and observing the change in the \( Y \). For propagation of
statistical error in $S(q)$ to fits parameters of the PDF, each measurement in $S(q)$ was varied within its statistical uncertainty and the resulting change in the fit was observed. The uncertainty contribution from each point in $S(q)$ is then given by,

$$
\delta Y_{\text{Stat}} = \sqrt{\sum_{i}^{i_{\text{max}}} \left( \frac{\partial Y}{\partial S(q_i)} \delta S_{\text{Stat}}(q_i) \right)^2}.
$$

(3.46)

The uncertainty due to corrections is similarly determined numerically by the formula

$$
\delta Y_C = \sqrt{\sum_{\text{All}} \left( \frac{\partial Y}{\partial C} \delta C \right)^2}.
$$

(3.47)

In addition to statistical and correction error, the uncertainty in the information content beyond $q_{\text{max}}$ contributes to the uncertainties in fits.

If the coordination shells are approximately Gaussian (as is the case for amorphous materials) the high-$q$ behavior is expected be oscillatory and have a Gaussian decay to zero [44]. The most natural discretization of the sine transform is to break the integral into half periods of this high $q$ oscillation, $T$, allowing Eq. (3.43) to be rewritten as

$$
G(r) = \frac{2}{\pi} \sum_{n=0}^{\infty} \int_{(n+1)T/2}^{(n+1)T/2} q \left[ S(q) - 1 \right] \sin(qr) dq.
$$

(3.48)

By formulating the sine transform of the structure function as a convergent series the final term in the summation may be treated as a tolerance in the calculation. The uncertainty in fit due to truncation is approximated as the change in the fit from truncation of $S(q)$ by an additional half period,

$$
\delta Y_{\text{Trunc}} = \left| \left( \frac{\partial Y}{\partial q_{\text{max}}} \right)(q_{\text{max}} - T/2) \right| / \sqrt{3},
$$

(3.49)
where the factor of $1/\sqrt{3}$ is the conversion factor from tolerance to standard deviation. For the amorphous Vitreloy 106a, $T/2 = 1.8 \, \text{Å}^{-1}$ at $17 \, \text{Å}^{-1}$. Total uncertainties in peak positions and heights are reported to one standard deviation.

### 3.2.4 Results and Discussion

The diffractions patterns measured at each position show marked asymmetry in the detector images. The two-dimensional scattering pattern from the image detector scaled to the intensity of the first peak in $I(q)$, when the X-ray beam incident on the sample at position 2 (Fig. 3.10), is shown Fig. 3.13.a. This pattern is calculated after background, gain, geometric, oblique and polarization corrections so that any asymmetry can be attributed to absorption and secondary scattering. Upon rescaling the detector image to high-$q$ intensities, this asymmetry is evident (Fig. 3.13.b).

![Two dimensional scattering pattern](image)

**Figure 3.13:** Two dimensional scattering pattern on the area detector for Vitreloy 106a, with the X-ray beam incident on the sample at position 2 (see Fig. 3.10): (a) scaled to the intensity of the first peak in $I(q)$ and (b) scaled to the intensity at high-$q$ to emphasize the asymmetry in the scattered intensity due to off-axis transmission.

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To more clearly demonstrate the intensity gradients, the intensity of each pixel in the diffraction pattern is divided by the angular-averaged intensity at a given scattering angle, \(2\theta\), i.e. \(I(2\theta, \phi)/\oint d\phi [I(2\theta, \phi)/2\pi]\). As shown in Fig. 3.14, the intensity gradients in this normalized pattern are in excellent agreement with those predicted from the spherical self-absorption and secondary scattering corrections discussed earlier, although small deviations are observed at high angles when the X-rays were incident far from the central axis of the sample (positions 1 and 5, Fig. 3.10). This is likely due to the curvature of the sample at the edge, which causes a breakdown in the small beam approximation that was made in calculating the corrections. The relative coordinates used for calculating the detector asymmetry in Fig. 3.14 were determined from best fits of the experimental asymmetry predicted by the self-absorption correction [2]. These fits gave precisely the same coordinates as determined by transmission measurements, validating this approach.

When all corrections are applied, the diffraction measurements at all of the positions in Fig. 3.14 give statistically equivalent structure functions up to a momentum transfer of 17 Å\(^{-1}\). Representative \(S(q)\), \(G(r)\) and \(g(r)\), determined at one position are shown in Fig. 3.15. The high degree of linearity observed at the low-\(r\) region of \(G(r)\) suggests that there is little systematic error in the analysis [37].
Figure 3.14: The measured and calculated intensity gradients when the X-rays are incident on the sample. The positions where the X-rays are incident on the sample are shown on the right hand side of the figure.
Figure 3.15: Measured (a) $S(q)$, (b) $G(r)$, and (c) $g(r)$ for the Vitreloy 106a amorphous sample after applying all corrections for spherical samples.
The peak positions and intensities from fits to the peaks in $S(q)$ and $g(r)$ are listed in Table 3.3. The shoulder on the high-$q$ side of the second peak in $S(q)$ is generally taken to indicate icosahedral short-range order (ISRO). The ratios of the peak positions $q(2^{\text{nd}})/q(1^{\text{st}}) = 1.69$ and $q(\text{shoulder})/q(1^{\text{st}}) = 1.96$ are within 5% of those expected for a perfect icosahedron (1.71 and 2.04 respectively) [45]. Based on this qualitative comparison and the similarity to reports from other Zr-based metallic glasses and liquids [46] and liquids [46, 47] it can be surmised that Vitreloy 106a is dominated by ISRO, consistent with Frank’s hypothesis [48].

Table 3.3: Positions and Magnitudes of the First Five Peaks in the Structure and Pair Distribution Functions for Vitreloy 106a.

<table>
<thead>
<tr>
<th>Peak</th>
<th>$S(q)$</th>
<th>$g(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position</td>
<td>Magnitude</td>
</tr>
<tr>
<td>1</td>
<td>2.606 ± 0.001</td>
<td>3.303 ± 0.005</td>
</tr>
<tr>
<td>1 Shoulder</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>4.405 ± 0.002</td>
<td>1.391 ± 0.002</td>
</tr>
<tr>
<td>2 Shoulder</td>
<td>5.105 ± 0.005</td>
<td>1.067 ± 0.002</td>
</tr>
<tr>
<td>3</td>
<td>6.395 ± 0.01</td>
<td>1.076 ± 0.002</td>
</tr>
<tr>
<td>4</td>
<td>8.27 ± 0.02</td>
<td>1.042 ± 0.002</td>
</tr>
<tr>
<td>5</td>
<td>10.11 ± 0.04</td>
<td>1.035 ± 0.002</td>
</tr>
</tbody>
</table>

The asymmetry in the first peak in $g(r)$ indicates the presence of two atomic distances. Since Zr is the largest constituent and has the dominant scattering cross-section, it is expected that Zr-based atomic pairs will dominate the behavior of $g(r)$. As for Cu-Zr [47], the two atom pair lengths in the first peak can be associated with Zr-Zr (high-$r$) and the Zr-solutes (low-$r$). That the maximum in the first peak in $g(r)$ ($r = 3.14$) corresponds to approximately twice the 12 coordinated radius of zirconium ($2r_{CN12} = 3.2$) [49] is consistent with this assessment.

As was the case for $S(q)$, the ratio of peak positions is consistent with ISRO. As shown in Fig. 3.16, the ratio of the nearest neighbor separation between vertices in a perfect icosahedron to the second nearest vertex is 1.62. The ratio of the first peak position in $g(r)$ to the
second peak position, $r(2^{nd})/r(1^{st})$, is equal to 1.65. This is consistent with solute-centered icosahedral clusters with Zr vertices. The ratio of the vertex to the center distance (low-$r$ shoulder) to the nearest neighbor vertex separation (first peak position) is 0.95 for an ideal icosahedron (Fig. 3.16). However a ratio of 0.88 is observed. This discrepancy suggests a contribution from solute-solute bonding at low-$r$, which will create local atomic stress. The large atom fraction of solutes and the size mismatch among them may inhibit long range ordering of the icosahedra, preventing the nucleation of the icosahedral phase with rapid cooling and promoting glass formation in this bulk metallic glass-former.

Figure 3.16: Separation distances between atoms in an ideal icosahedron, normalized to the vertex to vertex nearest neighbor separation.
3.2.5 Conclusion

Quantitative synchrotron scattering studies are now possible in containerless environments using a variety of levitation techniques, in particular aerodynamic, electromagnetic and electrostatic levitation. A review of the data analysis methods most relevant to such beamline levitation experiments has been presented. Based on room-temperature studies of a bulk metallic glass, Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ (Vitreloy 106a), recently reported calculations for self-absorption and secondary scattering corrections for spherical samples [2] have been confirmed. High quality measurements were obtained to 17 Å$^{-1}$. The errors in $S(q)$ and $g(r)$, which are often neglected in reports of diffraction studies, were presented for model parameters by uncertainty propagation of statistical errors, correction errors and, in $g(r)$, truncation errors. Finally, excellent agreement is found between an experimental and predicted asymmetry in the detector image when the X-rays impinge away from the center of the sample.

3.3 References


Chapter 4

The Specific Volume, Thermal Expansion, Kinetic Strength and Glass Forming Ability of High Temperature Liquids

In this chapter, the relationships between specific volume, thermal expansion, kinetic strength and glass forming ability are explored for metallic liquids in their equilibrium, supercooled liquid and glass states. Following a report correlating the density of the glass with GFA in the Cu-Zr alloy system [1], a systematic study of specific volume and thermal expansion coefficient was performed over the same compositional range, Cu$_{100-x}$Zr$_x$ ($30 \leq x \leq 54$). Thirty-eight compositions were measured, and it was found that thermal expansion correlates with GFA, Sect. 4.1 [2]. The interpretation of these results rested on two assumptions: (i) that GFA correlates with kinetic strength and (ii) that the thermal expansion coefficient changes with temperature.
In Sect. 4.2, another systematic study over Cu$_{100-x}$Zr$_x$ ($30 \leq x \leq 54$) liquids, looking at viscosity as a function of temperature, confirmed the correlation between GFA and kinetic strength [3]. The temperature dependence of thermal expansion coefficient was not measurable in the Cu-Zr system due to their poor GFA. However, measurements of thermal expansion through glass transition in Zr$_{57}$Cu$_{15.4}$Ni$_{12.6}$Al$_{10}$Nb$_5$ and Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ liquids were performed (Sect. 4.3) [4]. This study identified a temperature-dependence in the thermal expansion coefficient, which appeared to depend on the kinetic fragility of the liquids, as predicted.

At the time of this writing, Sect. 4.1 is published in *Physical Review Letters* [2], Sect. 4.2 is in review with the *Journal of Non-Crystalline Solids* [3], and Sect. 4.3 is in review with the *Journal of Applied Physics* [4].

4.1 Volume Expansion Measurements in Metallic Liquids and Their Relation to Fragility and Glass Forming Ability: An Energy Landscape Interpretation [2]

4.1.1 Introduction

For many years following their discovery [5], the production of metallic glasses required rapid cooling or quenching of the liquids ($10^5$ to $10^6$ K/s) [5,6], significantly limiting their usefulness. Following earlier work [7], a new class of metallic glasses became available,
which could be prepared at slower cooling rates comparable to those used for the silicate glasses [6, 8]. Because of their ease of production and desirable physical properties, these glasses are increasingly finding technological applications [9, 10]. However, why some metallic liquids easily form glasses, while others do not, is a key unresolved question.

It is widely believed that the density of the liquid is linked to glass formability, since high-density liquids are taken to be thermodynamically more stable and to have a higher viscosity. Recently reported measurements of the relative densities of a series of Cu$_{100-x}$Zr$_x$ (30 ≤ x ≤ 54) glasses show this correlation [1]. The smallest density changes on crystallization, suggesting a more dense amorphous phase, were observed for Cu$_{50}$Zr$_{50}$, Cu$_{56}$Zr$_{44}$, and Cu$_{64}$Zr$_{36}$ [1], which are precisely the best glass forming compositions, as determined from the maximum dimensions that can be cast into the amorphous state (critical thickness) [1, 6, 11–15]. Here, we present the corresponding liquid data for the density and the volume expansion coefficient for 38 compositions of Cu-Zr. To within measurement error, no local density maxima were observed in equilibrium or supercooled liquids; instead, maxima in the thermal expansion coefficient were observed. This indicates that the structural evolution that leads to the higher density in the glasses must occur in liquids at intermediate temperatures, likely on approaching the glass transition temperature, $T_g$.

In addition to identifying a new method for finding the best glass forming compositions from properties of their liquids, these results shed new light on the relation between the fragility classification (strong or fragile) for liquids [16] and their expansion coefficients at high temperatures. Liquids are strong when the temperature dependence of the response functions (viscosity, diffusivity, relaxation time, excess entropy of the liquid over that of the crystal, etc.) is Arrhenius over a wide temperature range. They are successively more fragile as these quantities show more non-Arrhenius (Vogel-Fulcher-Tammann, stretched
exponential, etc.) behavior. While there are some exceptions (e.g., Sorbitol, Salol), strong liquids, such as SiO$_2$, tend to be better glass formers than very fragile liquids; for metallic glasses, we are not aware of any exception to this trend [17–20]. In agreement with this trend, the density data for the Cu-Zr glasses [1], molecular dynamics (MD) simulations of the liquid viscosity [21], and diffusion coefficients [22], as well as viscous flow measurements near the glass transition [23], indicate that the best Cu-Zr glasses and their liquids are stronger.

Since theoretical studies have shown that the volume expansion coefficient also correlates with fragility, a larger expansivity near T$_g$ signals a more fragile liquid [24, 25]. It would, therefore, be expected that the best glass forming liquids will have a smaller thermal expansion coefficient, in addition to having a larger density and being stronger. The data presented here show that the reverse is true at higher temperatures, with stronger liquids having the larger expansion coefficient. As will be discussed, this is in agreement with energy landscape arguments, which suggest a crossover behavior (e.g., the expansivity of stronger glasses becoming larger than that of fragile glasses in the liquid state) at higher temperatures. For Cu-Zr, the data presented here show that this crossover temperature occurs between the $T_g$ and $2T_g$.

### 4.1.2 Experimental

Samples of Cu$_{100-x}$Zr$_x$ (30 ≤ $x$ ≤ 54) were levitated in high vacuum (∼ 10$^{-7}$ Torr) in an electrostatic levitation facility and were melted using a 50 W diode laser. The volumes of the liquids were determined as a function of temperature from the video images of the two-dimensional (2D) silhouette. The volume was computed by integrating the 2D image around an axis of symmetry (see Refs. [26–30] and Ch. 2 for more details).
Average volume as a function of temperature was obtained from multiple radiative cooling studies at each sample composition. A representative data set is shown in Fig. 4.1.a, and the specific volume (average volume per atom) calculated from the measured volume as a function of temperature is shown in Fig. 4.1.b. The coefficient of thermal expansion \[ \beta = (\partial \ln V/\partial T)_P \] was determined from linear fits to the volume-temperature data. The error in the absolute volume is dominated by the uncertainty in the volume and mass calibrations (±0.5% tolerance). These uncertainties cancel in the thermal expansion calculations. There, the dominant contributions to the error are the uncertainty in the temperature calibration (±1% tolerance) and the uncertainty in the linear fit to the data (≈ ±1% to 95% confidence), giving a total uncertainty in \( \beta \) of ≈ ±2%.

Figure 4.1: (a) Temperature (■) and specific volume (△) as a function of time for a Zr\textsubscript{46}Cu\textsubscript{54} liquid during a representative radiative cooling cycle. The abrupt temperature rise near 48 s is due to crystallization (recalescence). (b) Specific volume versus temperature curve during this cycle.
4.1.3 Results

The specific volume and thermal expansion coefficients of 38 Cu-Zr liquid compositions were measured over approximately 200 K above and 50 K below their liquidus temperatures, $T_l$. Since the relevant temperature for glass formation is $T_g$, for a meaningful comparison among all alloy compositions, the data are shown in Fig. 4.2 at a normalized temperature of $2T_g$. $T_g$ was estimated from a linear fit to the published data [31], using the relation $T_g$(K) = 866.48 - 3.91$x$, where $x$ is the atomic percent of Zr. The specific volume shows an approximately linear increase with increasing Zr, as would be expected from a rule of mixtures argument for an ideal system. The statistical error in the measured volume of the liquids limits the detection of a density fluctuation to within about 1%, which is approximately 3/4 of the magnitude of the largest peak reported in the glass density [1]. Within this error, no peaks are evident in the liquid density as a function of composition. In contrast with the volume data, however, statistically significant local maxima are observed in the thermal expansion.

To show the local maxima more distinctly, the normalized expansivity, $\beta_N$, are plotted in Fig. 4.3,

$$\beta_N = (\beta_{Exp} - \beta_{Cal}) / \beta_{Cal}, \quad (4.1)$$

where $\beta_{Cal}$ is the expected expansivity that follows the approximately linear trend with Zr concentration, calculated by assuming an ideal rule of mixtures based on the $\beta_{Exp}$ values for the highest and lowest Zr concentrations studied. Clearly defined peaks in $\beta_N$ are observed at 50.5, 43.5 abd 36 at. % Zr (Fig. 4.3), which are the compositions of maximum critical thickness (best glass formation) determined previously [1, 6, 11–15]. Although the data reported here are measured at $2T_g$, within a given composition $dV/dT$ was constant across the entire 250 K range.
Figure 4.2: Specific volume (△) and thermal expansion coefficient (■) of liquid Cu$_{100-x}$Zr$_x$ at twice their respective glass transition temperatures, $T_g$ (i.e., $2T_g$).

Figure 4.3: Normalized liquid thermal expansion from the present measurements (■) and the critical casting thickness (△, taken from Ref. [1]) of Cu-Zr liquids.
Some correlations between volumetric properties and glass forming ability (GFA) in metal alloys have been suggested previously [32–38]. However, the reported correlations between expansivity and GFA are inconsistent and sometimes contradictory [36, 38]. It is crucial to note that these correlations are deduced from studies of liquids containing different elements, with different baselines and different anharmonicities. In contrast, the results presented here were obtained by systematically changing composition within the same alloy system, yielding the first clean correlation between liquid thermal expansion and GFA.

4.1.4 Discussion and Conclusions

As noted previously, near \( T_g \) a large thermal expansion in the liquid is correlated with a high fragility, and hence anticorrelated with GFA. To understand why this correlation found near \( T_g \) conflicts with the one reported here for high temperature, it is necessary to see how properties evolve over the \( \approx 500 \) K between the liquidus and glass transition temperatures. The definitions of strength and fragility in the Angell scheme [16] and within the context of the energy landscape formalism [39] are also needed.

The strong or fragile definition in terms of the atomic mobility and thermodynamic properties has already been mentioned. The energy landscape provides a statistical mechanical way of understanding the origin of this behavior in terms of structure. The landscape is the potential energy surface formed by the \( 3N \) atomic coordinates in a \( 3N + 1 \) dimensional space. Within this formalism, atomic structures (configurations with qualitatively similar pair distribution functions) are found within low energy portions (basins) of the energy landscape [39]. The fragile-or-strong classification refers to the temperature dependence of the energy landscape sampling. Liquids that continue to favor the atomic structures associated with the glass
to higher temperatures are defined as strong, while liquids whose probability distributions rapidly “smear out” over the energy landscape with increased temperature are defined as fragile [16]. These considerations define three distinct temperature regimes for liquids: (i) a low temperature region where basin occupancy is fixed and changes in the average structure are dominated by vibrational effects; (ii) a high temperature region where the entire energy landscape is sampled so that changes in the aggregate structure are dominated by Boltzmann statistics; and (iii) a transitional temperature range where neither are dominant. These correspond to the landscape dominated flow, free diffusion of atoms, and the landscape-influenced flow, as identified by Debenedetti and Stillinger [40].

The absence of density maxima in the equilibrium liquids suggests that near the liquidus temperature the Cu-Zr system is approaching the highly fluid temperature regime corresponding to a “smeared out” average structure [40]. The peaks in thermal expansion show that the better glass forming liquids approach their high-density glassy state more rapidly with cooling (as expected for stronger liquids) than do liquids of nearby compositions.

Based on these considerations, the relationship between thermal expansion and fragility then depends on the temperature region in which the thermal expansion coefficient is measured. As noted by Stillinger and Debenedetti, in liquids and glasses the temperature dependence of the volume expansivity can be separated into two parts: (i) “vibrational changes,” within a configurational basin, and (ii) “structural changes,” i.e., changes in the probability distribution among the basins. In the landscape dominated region, the temperature dependence of the expansivity in the amorphous solid is determined only by the vibrational contribution [24]. As for crystal solids, this is governed by the anharmonicity of the atomic potential. Upon heating to just above $T_g$, the vibrational properties of the glass remain manifest in the supercooled liquid [25,41]. Additional contributions from rapid structural changes in the
liquid increase the expansion coefficient. Therefore, a fragile glass shows a higher thermal expansion coefficient in the supercooled liquid just above $T_g$ than a stronger glass [24, 42]. In contrast, in the free diffusion high temperature range, the landscape becomes of marginal importance, blurring the meaning of a fragility distinction.

It is less clear what happens at intermediate temperatures, in the landscape-influenced regime. While the expansion coefficient for a fragile liquid is larger near $T_g$, the Cu-Zr data presented here show that it is smaller in the landscape-influenced regime, indicating that a crossover occurs. All of the Cu-Zr liquids are fragile; those compositions associated with the maxima in expansivity are just less fragile (hereafter referred to as stronger to avoid confusion). To understand the results presented here, then, it is useful to examine how the energy landscape (depth and degeneracy of the basins) changes for such liquids of similar composition but slightly different fragilities. As illustrated in Fig. 4.4.a, the stronger liquids have a larger number of low energy glasslike configurations than do the more fragile liquids, making them thermodynamically more stable. This stability is reflected by the wider temperature range over which the stronger liquids have smaller fractions of excited states (Fig. 4.4.b), corresponding to a smaller number of configurations and a wider landscape influenced region. In Fig. 4.4.c, this is reflected in the more gradual increase in shear viscosity on approaching $T_g$ for a stronger liquid, versus the sharper rise in viscosity near $T_g$ in the more fragile liquid (shown in an Angell plot).

Since the probability distribution among basins changes most in the landscape-influenced region, properties of the liquid that are configuration-dependent, such as enthalpy and volume, will also undergo large changes. The derivatives of these quantities, i.e., specific heat and thermal expansion, each have a maximum within this region, followed by a crossover at higher temperatures when liquids with different fragilities are compared (Fig. 4.4.d). The
Figure 4.4: Interpretation of the distinction between “fragile” (thick black lines) and “stronger” (less fragile, thin red lines) liquids of similar composition in terms of (a) the topology of the energy landscape (adapted from Refs. [16, 40]), (b) the temperature ($T$) dependence of the fraction of thermally excited configurations (adapted from Ref. [16]), (c) the Arrhenius representation of liquid viscosity (Angell plot), and (d) second derivatives of Gibbs free energy (i.e., specific heat and thermal expansion). A crossover is evident at an intermediate temperature.

sudden increase and a maximum just above $T_g$ are common features of all liquids, where the rise correlates with fragility [43]. However, how these properties evolve in supercooled metallic liquids of different fragilities is not known from experimental data because of rapid crystallization. Interestingly, data for glycerol (a fragile liquid) [44] are consistent with these
energy landscape arguments. The experimental results reported here, along with the viscosity data at high temperatures [45], then indicate that the Cu-Zr liquids must be on the high temperature side of the landscape-influenced regime at $2T_g$.

A simpler qualitative explanation can be given in terms of entropy and volume fluctuations [46] in the supercooled liquid above $T_g$. The volume expansion coefficient is proportional to the cross fluctuation terms in volume and entropy, $\langle \delta V \delta S \rangle$, corresponding to an infinitesimal change in temperature, $\delta T$. The excess entropy and volume of a fragile liquid over that of the corresponding crystal phase increase much more rapidly above and near $T_g$, compared to a strong liquid [47]. Therefore, the expansion coefficient of a fragile liquid is expected to be large just above $T_g$. Thereafter, it should decrease more rapidly with increasing temperature than for a stronger liquid. This naturally leads to a crossover temperature, above which the fragile liquid will have a smaller expansion coefficient than a stronger liquid, in agreement with the energy landscape argument and the experimental observation. Consistent with evidence from other studies, then, stronger liquids are the best glass formers in Cu-Zr. Those liquids will have a larger thermal expansion coefficient at high temperatures, which is opposite to what might be expected based on considerations made near the glass transition temperature, below the crossover temperature.

To our knowledge, this is the first comparative study of changes in the thermal expansivity as a function of composition and what they reveal about fragility in supercooled and equilibrium liquids within the same chemical system. By confining the studies to the same chemical system, obfuscations from differences in chemical bonding and anharmonic contributions to the potential, which can dominate the behavior of the expansivity, are avoided. As a result, a cleaner correlation between the thermal expansion of the liquid at high temperature and glass formability has been established. The narrow composition range over which peaks
in the expansivity are present indicates that the structural features that lead to better glass formation are strongly composition dependent. The experimental results presented here suggest that an extension of modeling efforts to focus on correlations between physical properties (such as the expansivity) and the kinetic and thermodynamic fragility of the high temperature liquids will lead to new predictive methods for glass formation and a deeper understanding of the meaning of liquid fragility.

4.2 Correlation Between Kinetic Strength, Volumetric Properties, and Glass Forming Ability in Metallic Liquids [3]

4.2.1 Introduction

Since the discovery that metallic alloys could be cooled and held below their equilibrium melting temperature (supercooled) [48, 49], volume and atomic packing have played central roles in the theories used to describe these systems. From Frank’s hypothesis [50], to Turnbull, Cohen and Grest’s free volume models [51, 52] and more recently Miracle’s packing model [53], dense packing has been identified as a key reason for greater thermodynamic stability and slower kinetics in liquids. Although atomic packing in amorphous phases has been correlated with critical casting thickness [1], an empirical connection to the dynamics of the liquid and volume has not been reported previously. Here, we present a systematic study of the viscosity of Cu$_{100-x}$Zr$_x$ ($30 \leq x \leq 55$) liquids, establishing relationships between the volumetric properties of the liquid, the kinetic fragility, and the glass forming ability (GFA).
The unifying concept of strength/fragility, first proposed by Angell [16], has played an important role in understanding the thermodynamic and dynamical properties of glass forming liquids for many diverse materials classes (organic and inorganic compounds, metallic alloys, colloids). Liquids are kinetically “strong” when the temperature dependence of the response functions (viscosity, diffusivity, relaxation time etc.) follows an Arrhenius behavior. They are “fragile” when these quantities show a non-Arrhenius (or super Arrhenius) behavior with temperature. The degree of non-Arrhenius behavior of the viscosity, $\eta$, can be parameterized by fits to the Vogel-Fulcher-Tammann (VFT) equation,

$$\eta = \eta_0 \exp \left[ \frac{D^* T_0}{(T - T_0)} \right], \quad (4.2)$$

where $\eta_0$ is the viscosity in the infinite temperature limit, $T_0$ is the temperature at which the viscosity becomes infinite, and $D^*$ is a measure of the fragility of the liquid, called here the kinetic strength, to differentiate if from the commonly-used fragility index, which is defined near the glass transition temperature. As $D^*$ increases the VFT equation becomes more Arrhenius, consistent with a stronger (less fragile) liquid [43].

The empirical rule, for metallic liquids, that strength correlates with glass formability is reasonable, since stronger glasses have higher viscosities at high temperatures, which inhibit the nucleation and growth kinetics [20]. There are, however, exceptions to this rule. For example, Zr$_{57}$Cu$_{15.4}$Ni$_{12.6}$Al$_{10}$Nb$_5$ (Vitreloy 106) requires a higher cooling rate to form a metallic glass than Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ (Vitreloy 106a) [34, 54] despite being the kinetically stronger of the two liquids [55]. This occurs because, the local order in the liquid in the former case is more similar to that of the primary crystal phase [56], which decreases the nucleation barrier and promotes crystallization.
Density provides a measure of the degree of local or medium range order in a liquid because of the positive correlation between energy and volume in metallic systems. Maxima in the density of the glass [1] and the thermal expansion coefficients of the liquid [2] at the best glass forming compositions in CuZr alloys (i.e., Cu$_{50}$Zr$_{50}$, Cu$_{54}$Zr$_{44}$ and Cu$_{64}$Zr$_{36}$ [1, 6, 11–15]), corresponding to presumed minima in the internal energy of the glasses, were therefore interpreted as manifestations of strong liquid behavior. However, in the absence of experimental data for viscosity and diffusivity, this could not be verified. The viscosity data reported here for 30 Cu$_{100-x}$Zr$_x$ ($30 \leq x \leq 55$) equilibrium and supercooled liquid alloys provide a direct verification of that interpretation. Peaks in kinetic strength were observed for the best glass forming compositions, confirming the inverse correlation between fragility and GFA.

4.2.2 Experimental

Master ingots of approximately 1 g for each composition were prepared by arc-melting high-purity Cu (99.995%) and Zr (99.9+% with nominal 3% Hf) in stoichiometric quantities. The arc-melting was performed in a high-purity Ar gas atmosphere (99.998%) after at least three cycles of evacuation (to less than 100 mTorr) and Ar gas backfilling of the chamber. Samples of mass 70-90 mg were prepared from portions of the master ingots by additional arc-melting. These samples were levitated and melted in an electrostatic levitation facility under high vacuum ($\sim 10^{-7}$ Torr) [27]. By levitating the sample in vacuum, heterogeneous nucleation catalyzed by contact with air and/or the container is avoided, allowing for data be to acquired in the supercooled liquid [27, 57]. The temperature was measured using a Metis MQ22 two-color ratio pyrometer (Process Sensors Corp.), operating at 1.40 and
1.64 µm wavelengths. The viscosity at each temperature was measured by oscillating drop technique [58, 59].

In brief, the oscillating drop technique was used to determine the viscosity by modulating the levitation electric field near the $l = 2$ resonant frequency (120-140 Hz) of the liquid to induce surface vibrations. The surface deformation was captured by high speed (1560 frames per second) video of the sample’s silhouette. Intensity integration of each video frame varied in proportion to the amplitude of the second harmonic. After the perturbation was removed, the amplitude of the surface harmonic oscillations damped exponentially, with a time constant inversely proportional to the viscosity [60]. A representative intensity signal, decaying due to viscous damping, is shown in Fig. 4.5.

![Figure 4.5: Viscous damped surface oscillations recorded for a Cu$_{56.5}$Zr$_{43.5}$ liquid at 1200 K.](image-url)
The viscosity was measured as a function of temperature and liquid composition during slow cooling, Fig. 4.6. Since the oscillating drop technique only allows the viscosity to be measured over a limited, low viscosity, range, fits to the VFT equation (Eq. 4.2) are overparameterized. This results in unphysical $T_0$ values (i.e., $T_0 \gg T_g$) and artificially reduces $D^*$. Because Cu-Zr liquids are fragile, since $T_0 \to T_g$ with increasing fragility [61], and since the measurements were made at high temperatures, an approximate form of the VFT equation can be used,

$$\eta \sim \eta_0 \exp \left[ D^* T_g / (T - T_g) \right] \text{ as } (T_g - T_0) / T \to 0,$$

mitigating the problems with $T_0$.

Figure 4.6: (a) The viscosity ($\triangle$) of Cu$_{56.5}$Zr$_{43.5}$ as a function of $T_g / T$, $T_g = 696$K and a fit to Eq. 4.3 (line); (b) the cooling curve during which damping time measurements were made.
The modified VFT fit now has the same number of free parameters as an Arrhenius fit, but with lower residuals. Due to this approximation, however, the values of $D^*$ are expected to be systematically lower than those obtained from fits over a wider viscosity range, but trends across composition are maintained. For the fits to the Cu-Zr data, $T_g$(K) = 866.48 − 3.91$x$ (linear fit to [31]), where $x$ is the atomic percent of Zr [2]. An example of the quality of the fit is shown for the Cu$_{56.5}$Zr$_{43.5}$ data in Fig. 4.6.a. Because of the exponential dependence on temperature, the error in absolute viscosity is dominated by the uncertainty in the pyrometer calibration ($\pm$10% tolerance). The error in $D^*$ is less sensitive to the temperature calibration (approx. $\pm$1% tolerance), while it is more sensitive to the confidence interval of the linear fit (approx. $\pm$2%), giving a total uncertainty in $D^*$ of approx. $\pm$2%. The additional scatter observed in the data are likely artifacts from the functional form used in the fits.

4.2.3 Results and Discussion

The viscosities were measured within the temperature range 1100-1300 K (approx. 0.01-0.1 Pa-s). Because the liquidus temperatures vary significantly across the alloy series, a meaningful comparison of the viscosities and the temperature dependence of the fit parameters as a function of composition can be made only at some reference temperature. Since within an Angell plot the relevant temperature is $T_g$, the viscosities are compared at a common temperature of $T_g/T = 0.6$ in Fig. 4.7. The viscosity shows a nearly monotonic increase with increasing Zr concentration, which does not correlate with the GFA. In contrast, $D^*$, derived from fitting Eq. 4.3 to the experimental data, show local maxima at 36, 44 and 50 at. % Zr, which are precisely the compositions of maximum critical thickness (best glass formation) [1], as shown in Fig. 4.8.
Figure 4.7: The viscosity (red △) and $D^*$ (■) for Cu$_{100-x}$Zr$_x$ liquids at $T_g/T = 0.6$.

Figure 4.8: The kinetic strength, parametrized by $D^*$, from the present measurements (■, lines inserted to guide the eye) and the critical casting thickness (red △, taken from ref. [1]) for Cu-Zr liquids.
The experimental dynamical and volumetric correlations with GFA for Cu-Zr alloys from this study and others are summarized in Table 4.1. The results presented here allow the volumetric properties to now also be correlated with strength.

Table 4.1: Measured Correlations with Strong or Fragile Behavior in Cu-Zr Liquids.

<table>
<thead>
<tr>
<th>Kinetic Strength, $D^*$</th>
<th>GFA</th>
<th>Temperature Range</th>
<th>Viscosity, $\eta$</th>
<th>Density, $\rho$</th>
<th>Thermal Expansion, $d\ln (\rho) /dT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>High$^a$</td>
<td>Near $T_g$</td>
<td>No Study</td>
<td>High$^c$</td>
<td>No Study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Above $1.6T_g$</td>
<td>Uncorrelated$^a$</td>
<td>Uncorrelated$^b$</td>
<td>High$^b$</td>
</tr>
</tbody>
</table>

$^a$This work, $^b$[2], $^c$[1]

Although the kinetic strength of the liquid, the density of glass and the thermal expansion coefficient of the liquids were all independently correlated with GFA, it is more appropriate to consider these volumetric properties and GFA as manifestations of the kinetic strength. At high temperatures stronger liquids are expected to develop structural order at a higher rate than more fragile liquids. In systems where volume and energy have a positive correlation this is manifest as a higher thermal expansion coefficient [2]. Although this correlation is expected to reverse near the glass transition [24,25,42], it is expected that a stronger liquid will be more ordered than a fragile one. The additional order in the strong liquid is manifest as a larger density near the glass transition temperature and in the amorphous phase [1]. The better-established order of the stronger liquid would raise the nucleation barrier of crystal phases that may form if they have a structure different from the liquid and decrease the growth rate due to an increase in the viscosity, both favoring glass formation. This would explain the observed correlation of the density and thermal expansion coefficient with GFA in the Cu-Zr liquids.
4.2.4 Conclusions

A systematic study of the viscosity of equilibrium and supercooled Cu\textsubscript{100-x}Zr\textsubscript{x} liquids (30 ≤ x ≤ 55) showed no correlation between the viscosity of the liquid at $T_g/T = 0.6$ and the glass forming ability. However, peaks in the kinetic strength were observed at the best glass forming compositions, confirming in these liquids the empirical rule that stronger metallic liquids are better glass formers [20]. The new experimental results validate earlier studies of volumetric properties [1, 2] of these alloys and establish a clear connection between GFA, the volumetric properties of the liquid and glass, and the kinetic strength.

4.3 Measurements of Volume, Thermal expansion, and Specific heat in Zr\textsubscript{57}Cu\textsubscript{15.4}Ni\textsubscript{12.6}Al\textsubscript{10}Nb\textsubscript{5} and Zr\textsubscript{58.5-}\Cu\textsubscript{15.6}Ni\textsubscript{12.8}Al\textsubscript{10.3}Nb\textsubscript{2.8} Liquids and Glasses [4]

4.3.1 Introduction

For both thermodynamic and kinetic reasons the specific heat ($C_p$) and the thermal expansion coefficient ($\alpha$), play important roles in glass formation. The excess enthalpy and entropy of the liquid over the crystal phases, obtained from the enthalpy and entropy of fusion and the excess $C_p$, determine the driving free energy for crystal nucleation and growth [62]. A metastable glass is obtained during cooling the liquid from high temperature when the nucleation and growth of the lower-energy crystalline phases are kinetically inhibited. The free volume model [51, 52, 63] is often invoked to explain the dynamical properties (viscosity,
diffusivity, structural relaxation) of the supercooled liquid. Within these models, the amount of free volume is related to the thermal expansion coefficient, making it an important kinetic parameter.

We recently demonstrated in Cu-Zr liquids that the thermal expansion coefficient of metallic liquids correlates with glass formability, with the best glass forming liquids having a larger value of $\alpha$ near the liquidus temperature ($T_l$) than nearby compositions [2]. The concept of fragility is often used to characterize glass forming liquids, where the rate of change of a dynamical property such as the viscosity is larger near the glass transition temperature ($T_g$) for more fragile liquids [16]. This is typically taken to mean that the rate of change of the structure of a more fragile liquid is also greater near $T_g$. The thermal expansion results, then, were in apparent contradiction with the general perception in the metallic glass community [20] that better glass formers are stronger liquids. This apparent contradiction can be reconciled if $\alpha$ is temperature dependent and if the $\alpha(T)$ for strong liquids cross those for more fragile liquids at some intermediate temperature between $T_l$ and $T_g$ [2]. To confirm this requires a measurement of $\alpha(T)$ in metallic glass-forming liquids over the entire supercooled liquid region down to $T_g$.

Although considerable amount of data are available for $C_p$ and $\alpha$ for the conventional oxides [64] and many inorganic and organic liquids (see [44,65,66]), very few measurements have been reported for supercooled metallic-glass-forming liquids. In most cases, these properties are measured either near $T_g$, or above/near $T_l$; rapid crystallization makes it very difficult to measure them in the deeply supercooled liquids. While specific volume measurements over the entire supercooled range from $T_l$ to $T_g$ have been reported in a few bulk metallic glasses (BMGs), such as Pd$_{40}$Ni$_{40}$P$_{20}$ [67], Pd$_{43}$Ni$_{10}$Cu$_{27}$P$_{20}$ [68] and Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10.0}$Be$_{22.5}$ (Vitreloy 1) [69], these data are not of sufficient precision to determine the temperature
dependence of $\alpha(T)$. The specific heat data for the entire supercooled range are equally sparse for the metallic-glass-forming liquids [69,70]. Here, we present the first measurements of $\alpha(T)$ for two such alloys, Zr$_{57}$Cu$_{15.4}$Ni$_{12.6}$Al$_{10}$Nb$_5$ (Vitreloy 106) and Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$-Al$_{10.3}$Nb$_{2.8}$ (Vitreloy 106a), from above $T_l$ to below $T_g$. The ratio $C_p(T)/\varepsilon$, where $\varepsilon$ is the total hemispherical emissivity, was also measured for the first time over such an extended temperature range. These measurements were possible because of the remarkable glass forming ability of these liquids, characteristic of strong liquids, and the use of a containerless levitation technique [27,57].

The most important result is that $\alpha(T)$ for these strong glasses [20,55] indeed show a small temperature dependence in the supercooled states, as predicted earlier [2]. Additionally, in contradiction to a recent suggestion [71], no evidence for a liquid-liquid phase transition in the supercooled liquid was identified in either the specific heat or the volume.

### 4.3.2 Experimental Techniques

Master ingots of Zr$_{57}$Cu$_{15.4}$Ni$_{12.6}$Al$_{10}$Nb$_5$ (Vitreloy 106) and Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ (Vitreloy 106a) of mass approximately one gram each were prepared by arc-melting Zr (99.95%, < 10 ppm O), Cu (99.999%, 1.5 ppm O), Ni (99.995%, 9 ppm O), Al (99.999%) and Nb (99.95%, < 10 ppm O) in the appropriate amounts on a water-cooled copper hearth under a high-purity Ar (99.999%) atmosphere. Our experience and that of others [72] show that oxygen impurities play an important role in determining the amount of supercooling and the glass forming abilities of Zr-based bulk metallic-glass-forming liquids. The master ingots were broken and smaller portions (50-70 mg) were re-melted to produce approximately spherical samples.
The thermophysical properties of the alloy liquids were measured under high vacuum (≈ 10^{-7} Torr) in a containerless environment using an electrostatic levitation facility [27, 57]. The spherical solid alloy samples were heated to temperatures above \( T_l \) using a 50 W diode laser and cooled by turning off the laser. Absence of heterogeneous nucleation sites (container wall, gas molecules) enabled the retention of the supercooled liquid below \( T_g \). A small amount of crystallization (< 15% volume fraction) was observed on cooling to \( T_g \); this was likely surface crystallization. The remaining sample remained liquid with supercooling and transformed to a glass at \( T_g \). The specific volumes of the equilibrium, supercooled, and frozen liquid were measured by analyzing video images of the shadow of the spherical samples during cooling [28]. The pixel dimensions in the digital images were calibrated with grade 3, 1/8 inch diameter WC standard samples. Temperature measurements were made using a two-color ratio pyrometer at high temperatures (900-2600 K) and a single color pyrometer at low temperatures (1200-330 K). Pyrometer calibration was made by matching the largest heat signature observed in the ESL with the largest heat signature observed in differential scanning calorimetry (Setaram Instrumentation Labsys™ DTA/DSC) measurements.

Since the levitated samples are in a high vacuum environment, when the heating laser is turned off they cool by radiation loss following the relation

\[
C_p/\varepsilon = \sigma A \left( T^4 - T_0^4 \right) / (dT/dt),
\]

(4.4)

where \( dT/dt \) is the cooling rate at temperature \( T \), \( \varepsilon \) is the hemispherical emissivity, \( \sigma \) is the Stefan-Boltzmann constant, \( A \) is the sample surface area and \( T_0 \) is the room temperature observed by the sample [57, 73]. The time-temperature profiles (cooling curves) can be used to determine \( C_p/\varepsilon \) as a function of \( T \).
4.3.3 Results and Discussion

In the initial heating/cooling cycles the samples crystallized during cooling, indicated by a sharp rise in temperature (recalescence) in the time-temperature cooling curves. As the highest temperature was gradually increased, the recalescence moved to lower temperatures and became smaller with each cycle. No recalescence was observed when the sample was heated above a threshold temperature of about 1400 K; it cooled through the glass transition temperature to form an amorphous solid. This was confirmed during the next heating cycle, where a sudden rise in sample temperature was observed due to the enthalpy released during the glass to crystal transformation. Subsequent cycles did not require heating the sample above the threshold temperature to form a glass. The sample volume, thermal expansion, and specific heat of the equilibrium liquids, supercooled liquids, and glasses were measured during these cooling cycles. It should be noted that the effects of thermal cycling on glass formation were similar for both Vitreloy 106 and 106a.

The ratio \( C_p/\varepsilon \) and the specific volume (\( V \) per g) measured as a function of \( T \) for a Vitreloy 106 sample during one of the recalescence-free cooling cycles (Fig. 4.9.a) are shown in Fig. 4.9.b and Fig. 4.9.c. The shape of the \( C_p/\varepsilon \) curve, a slow rise that reaches a maximum immediately prior to the glass transition, is similar to that reported for a Zr\(_{41.2}\)Ti\(_{13.8}\)Cu\(_{12.5}\)Ni\(_{10.0}\)Be\(_{22.5}\) BMG [70]. An additional small rise and decrease between 800-900 K, above \( T_g \), indicates a small enthalpy release. Interestingly, no discernible anomaly is evident in either the cooling curve (Fig. 4.9.a) or the specific volume (Fig. 4.9.c) around this temperature range. Instead a small deformation of the sample is observed, manifest as a sudden increase in shape-asymmetry and scattering of the measured coefficient, \( a_3 \), of the Legendre polynomial (Fig. 4.9.d) that is used to fit the sample profile in the video.
images [28]. This feature and the anomalies in the derivatives of the enthalpy \( (C_p/\varepsilon) \) and the volume (the expansivity, shown later in Fig. 4.10.a), suggest the slow growth of a solid phase between 800 and 950 K. As indicated by the smooth extrapolation between the lower temperature \( C_p/\varepsilon \) and \( \alpha \) data, and those above this thermal event, the growth of this phase must have abated at lower temperatures.

Figure 4.9: A typical cooling curve for a Vitreloy 106 sample that formed a glass in the ESL. The corresponding measurements of specific heat (b), specific volume (c), and sample asymmetry (d) are shown.
If this feature is associated with partial crystallization, integration of local maximum in $C_p/\varepsilon$ between 800 and 950 K indicates 3 - 5 % of the Vitreloy 106 sample volume crystallized during this cooling cycle, while the rest remained amorphous. Similar estimates for the Vitreloy 106a place the crystal volume fraction there at approximately 10 - 15%. Apparently, the cooling rates achievable for these samples in the ESL (3 - 4 K/s around 900 K) are not sufficient to prevent some crystallization near the nose of the time-temperature-transformation curves [43,54]. Samples made from different starting materials with higher oxygen content showed a similar anomaly at higher temperatures that increased with increasing oxygen concentration. Samples containing 500 - 600 ppm or more of oxygen completely crystallized during cooling in the ESL. This demonstration of poorer glass formation in samples containing a greater oxygen concentration is consistent with earlier reports in Zr-based BMGs [72].

Within a single cooling cycle the specific volume decreases continuously with temperature down to $T_g$, where a change in slope is observed (Fig. 4.9c). With the good statistics obtained from multiple cycles, the binned specific volume data could be differentiated to obtain $\alpha(T)$. As shown in Fig. 4.10.a for Vitreloy 106 and 106a, these thermal expansion coefficients show a slight downward trend with decreasing temperature between 1200 and 950 K. The specific volume data can be described over the temperature range of 950-1200 K by the functions $V(T) = (0.1455 \pm 0.00045) \times 10^{-5}T + (3.75 \pm 0.7) \times 10^{-9}T^2$ for Vitreloy 106 and $V(T) = (0.1460 \pm 0.00046) \times 10^{-5}T + (7.88 \pm 0.9) \times 10^{-9}T^2$ for Vitreloy 106a, where the volume is expressed in cm$^3$/g and the temperature in K. Also shown in Fig. 4.10.b are the $C_p/\varepsilon$ data for the same cooling cycles. Sharp decreases in both $C_p/\varepsilon$ and $\alpha$ below 800 K are consistent with the glass transition temperature [43,54]. Secondary maxima in $C_p/\varepsilon$ and $\alpha$ near the temperature range of 800-950 K are attributed to a small fraction of crystal phase formation. Since the densities of the crystal phases are larger than those of the liquids, crystal phase formation results in a larger decrease in the sample
volume and, hence, larger values of $\alpha(T)$ in this temperature range. Different amounts of crystal phases in the two alloys obscure the comparison of discontinuities in $C_p/\varepsilon$ and $\alpha$ at $T_g$, which are often used as a measure of fragility in glasses [74].

Figure 4.10: Thermal expansion coefficient (a) and specific volume (b) in the equilibrium and supercooled liquids, and the glass for Vitreloy 106 (black ■) and 106a (red △).
The decrease in thermal expansion with decreasing temperature in the supercooled liquid and their difference for the two alloys merit some comments. In our earlier work, it was argued that the structural contribution to the thermal expansion coefficient increases with decreasing temperature on approaching $T_g$ because of a positive correlation between volume and energy [2]. However, an additional anharmonic vibrational component contributes to $\alpha$ [24].

The decrease in $\alpha$ with decreasing temperature may be interpreted as a decreased sampling of higher energy configurations, where the anharmonicity of the potential is greater. On cooling the liquid, then, changes in $\alpha$ are determined by the increased structural component at lower temperatures, which increases $\alpha$, and the decreased anharmonic component. Since these alloys have very similar compositions, it is reasonable to assume that the anharmonic component decreases at nearly the same rate for the two alloys. If this is true, differences in the rates of structural changes are likely responsible for the difference in the slopes of $\alpha$ between the two Vitreloy liquids. Since Vitreloy 106a is a more fragile liquid than Vitreloy 106 [55,56], the structural contribution becomes larger for Vitreloy 106a as $T_g$ is approached. This may explain the observed larger slope for $\alpha$ for Vitreloy 106a, which is consistent with an earlier suggestion for the behavior of more fragile liquids [2].

As mentioned earlier, a liquid-liquid transition has been suggested in Vitreloy 106 based on a measured hysteresis in the volume during heating and cooling cycles in the supercooled liquid [71]. Those studies were performed by first cooling the liquids to approximately 850 K, followed by rapid heating. During cooling the sample showed the usual volume contractions at a steady rate down to approximately 980 K, followed by a faster contraction down to approximately 850 K. During subsequent heating, the volume increased at nearly the same rate as during cooling up to approximately 980 K, followed by an anomalous plateau between 1000 and 1140 K, and an increase at a much faster rate between 1140 and 1240 K. The authors
pointed out that no crystallization event (recalescence) was observed during cooling and the hysteretic behavior was attributed to a liquid-liquid phase transition.

The results of similar experiments are shown in Fig. 4.11. As reported by Li et. al., a hysteresis is indeed observed in volume during cooling and heating. However, a different conclusion is argued here. The temperature-time curve measured during rapid heating of the supercooled liquid shows an exothermic process starting near 916 K, followed by an endothermic process ending at $T_l$ (black curve, Fig. 4.11.b). The endothermic process is identified as melting, marked by the abrupt decrease in sample asymmetry in the equilibrium liquid. The exothermic process is associated with crystallization from the supercooled liquid, because if crystallization had been averted no melt plateau would be evident. The crystallization released a sufficient amount of heat to raise the sample temperature to $T_l$ and slowed the rate of the volume increase with increasing temperature between 1000 and 1100 K (Fig. 4.11.a). On remelting of the sample, the specific volume increases sharply. The combined effects of crystallization and remelting creates a backwards L-shaped curve (red triangles, Fig. 4.11.a) in the specific volume as function of temperature. Li et al. reported a plateau in the volume with heating [71], while here the rate of increase slows but does not become zero. Both features are likely due to crystallization, with the differences arising from different amounts of crystallization during heating in the two experiments.
Figure 4.11:  (a) Hysteretic behavior of specific volume during heating the supercooled Vitreloy 106 liquid. (b) Signature of crystallization from the supercooled liquid during heating and subsequent melting in the time-temperature heating curve.

4.3.4 Conclusions

The first measurements of the volume expansion coefficient, $\alpha$, and specific heat ($C_p/\varepsilon$) are reported for the equilibrium, supercooled liquids, and glasses for two prototypical examples of bulk metallic glasses, Vitreloy 106 and Vitreloy 106a. Such measurements have not been possible previously by conventional techniques because of rapid heterogeneous nucleation and growth of crystals on the container walls from the supercooled metastable liquids. The measurements reported here were made possible by using the containerless technique of electrostatic levitation. The results for $\alpha(T)$ are consistent with a larger structural contributions for stronger liquids at temperatures much higher than $T_g$. Also, contrary to an earlier claim [71], no evidence is found for a liquid-liquid phase transition in Vitreloy 106.
4.4 References


[5] W. Klement, R.H. Willens, P.O.L. Duwez, Nature 187(4740), 869 (1960). DOI 10.1038/187869b0. URL http://dx.doi.org/10.1038/187869b0


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Chapter 5

Summary and Conclusions

This work is part of a larger endeavor to ascertain why certain metallic alloy compositions form glasses more easily than others. Answering this question is the first step to engineering new and better metallic glass forming alloys. In this dissertation, the development and application of thermophysical and structural property measurements of liquid metals using the Washington University beamline electrostatic levitator (WU-BESL) were presented. The purpose of this work was to establish and perform high quality measurements of liquid metallic alloys for better understanding of the relationship between the bulk properties of the liquids and their glass forming ability with access to the equilibrium and supercooled liquid states. When performed systematically across a wide range of compositions in the Cu-Zr alloy system, a clear connection was observed between the volumetric properties, kinetic fragility and glass forming ability (GFA) of these alloys.

In Ch. 2, WU-BESL’s ability to make optical measurements of temperature, density and viscosity were described. Temperature measurements are the independent variable for other measurements, but depend strongly on the calibration for accuracy. In Sect. 2.1, the use of a differential scanning calorimeter (DSC) for calibrating the WU-BESL optical pyrometers, along with propagation of uncertainties in this calibration to other measured properties, was
detailed. As for density and viscosity measurements, these measurements involve a complex video and signal analysis, which were adapted and improved upon from literature methods, as described in Sect. 2.2.

In Ch. 3, the correction and data reduction of X-ray diffraction measurements acquired during BESL experiments was described. An uncommon geometry for X-ray diffraction measurements is encountered in BESL experiments. This geometry is that of a small, high energy, X-ray beam transmitted off-center of a spherical sample. The self absorption and secondary scattering corrections for this geometry were derived in Sect. 3.1. Experimental verification of these corrections was presented in Sect. 3.2. Also detailed in Sect. 3.2 were other corrections and analyses for calculation of the structure and distribution functions in BESL experiments. This included a novel approach to propagation error from reciprocal space functions to real space functions.

In Ch. 4, the results of three studies exploring the relationships between specific volume, thermal expansion, kinetic strength and glass forming ability of high temperature metallic liquids were presented. The systematic application of the thermophysical properties measurements described in Ch. 2 to the Cu$_{100-x}$Zr$_x$ (30 $\geq$ x $\leq$ 54) system revealed maxima in thermal expansion (Sect. 4.1) and kinetic strength of the liquids (Sect. 4.2) at the best glass forming compositions. The energy landscape theory used to understand this result predicts a temperature dependence in the thermal expansion coefficient. This temperature dependence was predicted to depend on the kinetic strength of the liquid; a prediction that was verified by measurements in Zr$_{57}$Cu$_{15.4}$Ni$_{12.6}$Al$_{10}$Nb$_5$ and Zr$_{58.5}$Cu$_{15.6}$Ni$_{12.8}$Al$_{10.3}$Nb$_{2.8}$ liquids as they cooled through the glass transition (Sect. 4.3).

The results of the studies performed in Ch. 4 show that in the Cu-Zr system kinetic strength is the dominant factor for glass formation, over thermodynamic stability. Similar systematic
studies may be required to determine whether this is a general property of metallic systems. Further, if kinetic strength is the dominant property for GFA, why certain compositions are kinetically stronger than other compositions remains an open question. That GFA correlates with the properties of the equilibrium liquid suggests that a ‘from the liquid’ approach might shed new light on these questions. Certainly, the WU-BESL, despite the often complex analysis required for measurements, has proven itself a valuable tool for such studies.
Appendix A

Volume Analysis Algorithms

The following is a step-by-step description of the volume integration algorithms found in VideoVolume.vi. These integration algorithms, ‘Harmonics’ and ‘Numerical’, refer to methods of integration about an image’s axis of symmetry. The ‘Harmonics’ algorithm is the adaptation of the Bradshaw algorithm described in Sect. 2.2. The ‘Numerical’ algorithm was developed for more rapid image processing and is based on numerical integration. The basic analysis algorithm is, by necessity, the same for all volume integration programs:

1. Silhouette edge detection
2. Determination of the axis of symmetry
3. Volume integration by rotation about the axis of symmetry

The details of these operations depend on the programs, but the order cannot be altered since each step depends on the step before it. Although ‘Harmonics’ and ‘Numerical’ both share many of the same technologies (e.g., subpixel edge detection and edge-dependent thresholds), their procedures are sufficiently different that they will be described independently.
The algorithms described in Appendix A.1 and A.2 are iterated for each frame of a video file. In both algorithms, several regions in the images are defined at the first frame of a video and used for the remaining frames. These regions are: (1) the sample region, a region containing only sample intensity; (2) the background, a region containing only background intensity; and (3) the region of sample motion, an annulus within which the edges of the silhouette can be found for frames. These regions are either defined by the user at the start of VideoVolume.vi or are determined programmatically.

A.1 Harmonics

1. The threshold is estimated as half-way between the average pixel intensities of the background and sample regions.

2. Coarse edge detection is performed to reduce the candidate area for edge locations.
   (a) IMAQ Find Circular Edge VI, part of the NI Vision Development Module, is iterated twice.
      i. Estimate the center and radius of the silhouette.
      ii. Use the estimate of the center and radius as inputs for a rough estimate of edge locations.
   (b) The sum of the 21 by 21 pixel blocks, surrounding each coarsely determined edge, defines a candidate area for secondary edge detection.

3. Radial edge search
   (a) The average $x$ and $y$ positions, of previously determined edge points, approximate the location of the silhouette’s center.
(b) The origin is redefined as the silhouette center, and the edges are converted to polar coordinates, \((x, y) \rightarrow (r, \theta)\).

(c) The average radial position of each edge point is calculated, \(<r>\).

(d) Edge searches are carried out at evenly spaced angles, along line-profiles beginning at the origin.

i. The number of search directions is the integer number of pixels on the circumference of the silhouette, calculated as \(C = 2\pi <r>\).

ii. The spacing between the search angles is \(2\pi/C\) radians is shown in the Fig. A.1.

iii. Line profiles are calculated at each search angle, from the inner radius to the outer radius of the region of sample motion.

iv. The line profile is broken into three sections as shown in Fig. A.2.
Figure A.2: Section splitting of the line profile.

A. Sample profile, the section of the line profile between the inner radius of sample motion and the edge candidate area.

B. Edge profile, the section of the line profile within the edge candidate area.

C. Background profile, the section of the line profile between the edge candidate area and the outer radius of sample motion.

v. A profile specific threshold is defined for each edge search as halfway between the average intensity of the sample profile and the average intensity of the background profile.

vi. Starting from the inner radius of the edge profile, a search is performed for the first pixel with intensity greater than the threshold.

vii. The first two points higher than the threshold, and the last two points lower than the threshold, are stored in memory for subpixel edge detection.

4. Subpixel edge detection by cubic interpolation
(a) The four points determined by each edge search are combined with the points from the search at the angle above and below, giving a total of twelve points.

(b) For each edge the following procedure is used to determine the subpixel location.
   i. The intensity as a function of radius is fit to a cubic polynomial.
   ii. The intensity fit is set equal to the threshold value and solved.
   iii. The edge location is the real solution within the range of the polynomial fit.

(c) Each edge point is converted to non-integer Cartesian coordinates.

5. The radial edge search and subpixel edge detection are iterated twice.

6. Origin refinement

   (a) The origin is redefined as the silhouette center, and the edges are converted to polar coordinates, \((x, y) \rightarrow (r, \theta)\) (initially \(\theta = 0\) is 12 o’clock).

   (b) A sixth order Legendre polynomial is fit to the edge radii, \(r_{fit}(\theta) = \sum_{i=0}^{6} a_i P_i (\cos(\theta))\).

   (c) The square-root of the mean square error is evaluated, \(L^2 = \left( \sum [r(\theta) - r_{fit}(\theta)]^2 \right)^{1/2}\).

   (d) Two golden ratio searches are performed to minimize \(L^2\) error by varying the location of the origin.

      i. The origin is first varied perpendicular to the axis of symmetry, \((\theta = \pi/2)\).

      ii. The origin is then varied along the axis of symmetry, \((\theta = 0)\).

7. The final Legendre polynomial fit is integrated to calculate volume in cubic pixels,
   \[ V = \frac{2}{3} \pi \frac{\pi}{0} r_{fit}(\theta)^3 \sin(\theta) d\theta \] as shown schematically in Fig. A.3.
A.2 Numerical

1. The threshold is estimated as half-way between the average pixel intensities of the background and sample regions.

2. Beginning at the top row of the sample range of motion, each row of the image is a line-profile for edge detection, shown schematically in Fig. A.4.

3. Coarse edge detection

   (a) Starting from the left edge of each row-profile, an edge is found at a pixel intensity less than or equal to the threshold.

   i. If an edge is found, its position is recorded $x_1$.

   ii. If no edge is found, the next search line is incremented by 1 and coarse edge detection is repeated.
Figure A.4: The search directions for edges in the Numerical algorithm in a low resolution image (left) and higher resolution image (right).

(b) Starting from $x_1$ plus an offset $x_0$ (0.95% the previous separation between edges, minimum 2 pixels), and moving to the left, pixel intensities are compared to the threshold until an intensity greater than or equal to the threshold is found.

i. If a second edge is found, its position is recorded $x_2$.

ii. If no second edge is found, the offset may be too large. The following procedure is used.

A. Starting from the $x_1 + x_0$ pixel, and moving toward $x_1$, pixel intensities are compared to the threshold until an intensity less than or equal to the threshold is found.

B. If no second edge is found to outside of 2 pixels from $x_1$, the offset is set to 2. The next search line is incremented by 1 and coarse edge detection is repeated.

C. If a second edge is found, its position is recorded $x_2$. 149
4. Background adjusted edge detection

(a) Edge dependent threshold calculation

i. The row profile, ending 15 pixels left from \( x_1 \) and beginning at the far left, is averaged to calculate the left edge background intensity.

ii. The row profile, beginning 15 pixels right from \( x_2 \) and ending at the far right, is averaged to calculate the right edge background intensity.

iii. The right/left edge dependent thresholds are calculated as halfway between each edge background intensity and the user defined sample intensity.

(b) Coarse edge detection is repeated to determine \( x_1 \) and \( x_2 \) with edge dependent thresholds.

5. Subpixel edge detection

(a) The intensities of the six pixels surrounding \( x_1 \), the three pixels in the sample, and the three pixels in the background are fit to a cubic polynomial.

(b) The real root within the range of the fit is the subpixel edge location, \( x_1' \).

(c) The last two steps are repeated for \( x_2 \).

(d) The sample diameter along this row of the image is measured from the difference between the location of the two edges, \( D = |x_2' - x_1'| \).

6. Proceed to next row, repeating the steps from coarse edge detection

7. Diameter as a function of row (y-position), \( D(y) \), is used to calculate the rows differential volume, \( dV(y)/dy = \pi (D(y)/2)^2 \); this differential volume is shown schematically in Fig. A.5.
Figure A.5: (a) An image silhouette, (b) the edges of the silhouette detected by the Numerical algorithm, and (c) the volume integration method for the algorithm.

8. Differential volume is numerically integrated in $y$ using a Bodes rule algorithm, $V = \frac{\pi}{4} \int D(y)^2 \, dy$. 
Appendix B

Guide to Density Acquisition

Before and during an experiment, the ESL operator is responsible for the equipment set-up, camera acquisition setting, sample test conditions, and calibration standards. The following is a guide to WU-BESL operators for acquiring and analyzing high quality video for density and thermal expansion measurements. Although this may not be of interest to the general reader, these guidelines and techniques serve as a reference for future researchers.

B.1 Equipment

Density is measured in the ESL by recording video of a levitated sample’s shadow. The video is processed to identify the silhouette’s edges and then integrated about an axis of symmetry to calculate the sample volume. The first reported density measurements in an ESL were made at the Jet Propulsion Laboratory by Chung, Thiessen and Rhim using a broad spectrum backlight [1]. A change in backlight to the ultraviolet range was proposed by Ishikawa et al. for improved silhouette contrast [2]. The image processing algorithm was improved by Bradshaw et al. [3] for greater pixel resolution in volume integration.
The density measurement system used in the WU-BESL was based on one developed by Dr. Robert Hyers, University of Massachusetts, and Gustov Rustan, Iowa State University, utilizing the best practices of Chung and Ishikawa. Video is taken of levitated samples by a 1.3 Megapixel Gig-E CMOS pixeLINK\textsuperscript{TM} Monochrome Camera. A narrow band pass filter is held just before the camera inside a C to T thread adapter that connects to the lens system. The lens is a K2/SC Long Distance Video Microscope with a close focus objective capable of magnifications of 2.13X-0.71X and a working distance of 222-418 mm. The sample is backlit through the port opposite the camera and lens by a collimated (this can be interpreted as directional) microscope LED with total beam power of approximately 240 mW and a beam diameter of 37 mm. Prior to May 2012, the LED backlight and bandpass wavelengths were 455 nm and 450 nm $\pm$ 10 nm FWHM respectively. After the installation of the LEDs for positioning, this was changed to 590 nm and 590 nm $\pm$ 10 nm FWHM.

The backlight is mounted with horizontal, vertical and yaw adjustment. Pitch is fixed by the vertical mounting. Before measurements, these should be adjusted to maximize the homogeneity of the background intensity observed in the density camera. The LED backlights have texture that can be seen at low intensity; this is minimized by operating at the maximum power output. The camera lens system includes a variable aperture, which should be narrowed to improve the depth of field, and reduce the measured intensity to desired contrast. The camera optics are supported by three vertical posts. Rough vertical and horizontal alignment should be performed by adjusting all posts to minimize strain on the mounting equipment. Fine horizontal and vertical adjustments can be made with the camera support by changing the pitch and yaw of the camera compared to the lens system.

Should the camera optics need to be disassembled, the lenses, the camera and the bandpass filter may need to cleaned. This should ONLY be done with compressed air. The use
of cleaning solvents can leave watermarks on the optics, which are difficult to remove. If solvents must be used, dry with lens tissues (available from Thorlabs) and use compressed air to remove the tissue fibers.

B.2 Camera Settings

The camera settings that an ESL operator may change during operation are: exposure time, image size and frame-rate. The frame-rate is chosen to balance statistics with file size. For density measurements, 25 frames per second (fps) were determined to be sufficient to provide good statistics without excessive data. The image size must be large enough so that all frame to frame sample motion is contained, while cutting excessive background pixels. The image size of a typical density frame is approximately 600 by 600 pixels.

Of the three settings, the exposure time is the most important one for volume measurements in ESL, since it most directly influences the quality of images. The exposure time should be as short as possible in order to avoid blurring effects, while large enough to maintain good contrast between the sample and background. The integration algorithms described in Appendix A are incapable of accurately accounting for blurring, since the half-height method assumes a static object. An empirically determined upper limit on the exposure time, above which blurring is significant, was found to be 10 milliseconds. Conversely, exposure time must be long enough to achieve optimal contrast ($\approx 180$ out of 255).

The optimal contrast for density measurements was determined from the video of an electrostatically levitated brass sphere of diameter of $3/32'' \pm 0.001''$, taken at a frame rate of 10 frames per second for 60 seconds at exposures of 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0 and
0.5 ms. These exposures resulted in contrasts of 255, 225, 200, 170, 145, 115, 85, 60 and 40 on a 0-255 (8-bit) scale. At these frame rates and exposure times it is presumed that no significant change can occur in the sample; therefore, fluctuations between sequential frames are artifacts of the integration algorithm. To quantify this, for a comparison of the precision between integration methods and the optimal contrast settings, the autocorrelation function is used rather than the standard deviation. The discrete autocorrelation value between sequential frames is

\[ r(1) = \frac{\sum_{i=1}^{N-1} (Y_i - \bar{Y}) (Y_{i+1} - \bar{Y})}{(N-1) \sigma^2}, \]  

(B.1)

In a noiseless, rotating sample the standard deviation of the volume signal would be a factor of \(2^{-1/2}\) of the amplitude of the volume change from rotation. The autocorrelation value would approach one as the time between measurements approached zero. For a rotational period of 15 sec and a sample rate of 0.1 sec the maximum possible value is \(r(1) = 0.999\).

The autocorrelation value is a normalized quantity. To measure the absolute scatter due to the volume integration, the average square difference between sequential frames is used,

\[ \delta V = \sqrt{\frac{\sum_{i=1}^{N-1} (Y_i - Y_{i-1})^2}{2(N-1)}}. \]  

(B.2)

This is related to the autocorrelation value for large \(N\) using the expression \(\delta V \approx \sigma \sqrt{(1 - r(1))}\).

The autocorrelation value and the relative scatter in volume for a brass standard sphere at different contrasts, using the two integration algorithms described in Appendix A, is shown in Fig. B.1.

Two trends appear in Fig. B.1: (1), 'Harmonics' has a small but consistent improvement in precision over 'Numerical' and (2), the precision improves with contrast.
Figure B.1: Relative precision (open symbols) and autocorrelation (filled symbols) of ‘Harmonic’ (red △) and ‘Numerical’ (black □) volume integration algorithms for a 3/32” diameter brass standard with different background to sample contrast.

Precision is only one aspect of the measurement; accuracy is the other. Since edge detection is based on a half contrast threshold, it is plausible that the absolute integrated volume of a sample may depend on the contrast of the silhouette with the background. This was observed in illumination tests of a brass standard as shown in Fig. B.2.

The observed deviations from a constant integrated volume are easily explained. At low exposures, background inhomogeneities may artificially push out edges and increase the integrated volume. At high exposures, near saturation, the edges may no longer be spread over multiple pixels, and subpixel resolution is lost, resulting in an artificially decreased volume. The relatively flat region in the contrast between 100-200 provides the range over
Figure B.2: Changes in integrated volume as a function of background contrast, relative to the average volume of contrast from 100-200, of a 3/32" diameter brass standard using the ‘Harmonics’ integration algorithm (errors represent relative frame to frame precision at each contrast).

which these two effects are minimal. Therefore, to balance accuracy and precision the optimal contrast should approach but not exceed 200 out of 255.
B.3 Pixel Calibration

To acquire volume measurements in standard units, a calibration is required to determine the effective pixel size at the levitation magnification. The pixel calibration is performed by levitating a ball bearing of a known volume and using the integration algorithm to determine the volume in cubic pixels. The ESL operator must take care in performing this calibration or risk large inaccuracies in the measured density of the samples.

B.3.1 Calibration Grades

Commercial ball bearings are given grades for diameter tolerances and sphericity. The most relevant quantity fixed by the grade is the basic diameter tolerance, which sets the accuracy of the average diameter for any given ball. For grades of 200, 25, 10 and 3 this tolerance is 0.001”, 0.0001”, 0.0001” and 0.00003” respectively [4]. For BESL experiments in 2009 and 2010, brass 3/32” diameter spheres with a grade of 200 were used as standards. This led to errors dominated by the calibration for these experiments. In spring 2011, Tungsten-Carbide 3/32 diameter grade 3 spheres were adopted to reduce the error to the level of other effects.

B.3.2 Cleaning

Standards must be cleaned by agitation (this can be ultrasonic or rapid stirring) in methanol followed by drying with compressed air before loading into the ESL chamber. This cleaning procedure has produced consistently clean standards for density data acquired in 2011. Prior to the purchase of the grade 3 Tungsten-Carbide no cleaning procedure was used.
A representative graph of the integrated video volume with time for a visually inspected, but uncleaned, brass standard is shown Fig. B.3. The periodic oscillations in the volume integration of the brass standard are real effects caused by sample rotation. Although upon first inspection no features are readily observable, upon close inspection specks of contaminants less than 50 µm in diameter radius can be observed, as shown in Fig. B.4. The contaminants appear and disappear along the edge of the silhouette with periodicity equal to that of the integrated volume oscillations.

![Graph showing volume deviations from the mean over time](image)

Figure B.3: Numerical integration of 3/32” diameter brass standard using 10 fps frame rate and 2.5 ms exposure time.

This demonstrates the high sensitivity of the integration algorithms to even slight surface changes on the sample. For this reason care must be taken by the ESL operator to use only clean calibration standards for density standards or risk negating the quality of the grade.
Figure B.4: Edge contaminants capable of producing oscillations in integrated volume measurement.

B.3.3 Sample Position

Sample motion along the optical axis changes the magnification. The K2/SC with CF-1/B lens system has a magnification of approximately one at the standard working distance for ESL density measurements. Using the volume measured at the zero of the lateral potential field as the standard, the change in volume measured 1.2 mm away and 1.3 mm toward the density optics along the optical axis was 0.8% and -1.2% respectively. Assuming an approximately linear dependence between working distance and magnification, a 1.0 mm shift changes the volume by 0.8%. This variability in the magnification makes the volume measurements a function of sample position.

The standard levitation procedure is to hold samples in the zero of the horizontal potential. This zero may change with the size and density of the sample. Between a calibration standard and a test sample, the maximum horizontal variability between successive launches is approximately 0.5 mm (resulting in an error of 0.3% when uncorrected). While floating the calibration standard, alignment circles can be set on the visualization and density cameras. To reduce magnification uncertainty to the levels of the sample stability, the operator must
move the samples to within the alignment circles before collecting density video. Calibration
and alignment should be performed before and after every sample to verify the magnification
was constant during the experiment. This procedure is designed to reduce magnification
error to the levels of the sample stability $\approx 100\mu m$ on average.

Sample stability should also be on the mind of an ESL operator. Samples with poor stability
will produce poor density video. The sample stability is maximized when the heating power
is off. Additionally, this gives improved undercooling. This is why video analyzed for density
purposes is primarily from free cool measurements. The quoted stability of the ESL along a
horizontal axis is $45\mu m$ for a sample in free cool [5], resulting in a magnification stability of
$\approx 0.03\%$.

**B.3.4 Deposition**

Compositions with high vapor pressure elements may lose mass during ESL processing. A
highly sensitive indicator of mass loss from a sample is the darkening of the background
intensity due to the coating of the evaporated elements on the camera window. Though the
change in background intensity cannot be easily used to quantify the mass loss, it serves as an
indicator when the sample mass is changing, and therefore when the calculated densities of
different frames cannot be directly compared. In highly depositing samples, mass uncertainty
may contribute significantly to the absolute density, though by the time mass loss becomes
significant enough to impact density measurements multiple component samples may shift in
composition due to preferential vaporization. The ESL user should control the temperature
so that significant deposition does not occur. To some extent, however, small levels of
deposition may be accounted for in the analysis.
B.4 ESL Acquisition Software

Density video acquisition is incorporated into a LabVIEW™ graphical user interface, GUI. The WU-BESL acquisition GUI is written in LabVIEW™ 8.6 and requires the NI Vision development module. For incorporation of pixeLINK™ products into LabVIEW™, pixeLINK™ provides subVIs with software development kit. The variable settings for density acquisition in the LabVIEW™ GUI are described in this section. LabVIEW™ interface controls are printed in **bold** for clarity.

B.4.1 Frame Rate, Seconds of Video and Link to Save Data

Frame Rate is the user controlled save interval for the density video. The argument for high frame rates is that it allows for better precision through averaging and clearer observation of abrupt features. This argument is tempered by the large file sizes that result from a high sampling rate. Due to computer memory constraints, .pds File Size should be limited to about 330 Mb, or approximately 600 frames (this depends on the frame size). The file size limit within an experiment is averted by the Link to “Save Data” button which continuously creates new video files of length set by Seconds of Video. As long as both the Link to “Save Data” button and the temperature Save Data are ON, new video files will be created (Note: Time Stamp? must be ON to create multiple save files and to match density to temperature).

Breaking up density measurement into multiple save files creates an additional problem when processed video files are matched to temperature. The beginning time of each of video is only recorded to within 0.1 seconds. When the Seconds of Video is large (on the order 10
(secs) this uncertainty is negligible, but it may become significant for short video files. The file size and the need for long video times sets an upper bound on the **Frame Rate**. A **Frame Rate** of 25 fps and 20 **Seconds of Video** per file satisfy these requirements for a wide range of frame sizes (regions of interest).

### B.4.2 Region of Interest, ROI

The **Region of Interest** (ROI) control on the **Properties** tab of the GUI defines the camera view. The **.pds File Size** of a given video is approximately proportional to the number of pixels in the ROI. The ROI and exposure times determine the intrinsic camera speed and therefore set hard upper bounds on the **Frame Rate** within pixeLINK™. The **Region of Interest** should be as small as possible to limit the video file size, but large enough to contain the entire range of the sample silhouette’s motion. A typical sample has a diameter of approximately 400 pixels and a motion of at most 50 pixels to each side. A background area of approximately 50-100 pixels on each side is necessary for video analysis. A typical **Region of Interest** for a sample with a radius of 1.25 mm would have a width and height of approximately 700x700 pixels (1 pixel ≈ 6 μm, this is a 4.2 mm × 4.2 mm window).

There are three ways to change the ROI. The **Tighten ROI** button prompts the user to select a region within a still frame of the current ROI, which will be the new **Region of Interest**. This method is imprecise but intuitive. **Tighten ROI** only allows the user to select a smaller region. The **Expand to Full** button returns the ROI to the default full camera view [0,0,1280,1024]. The final way to modify the ROI is to manually enter numbers into the **Region of Interest** array and click **Change Settings**. This is the most reliable
way of selecting the same ROI between multiple experiments. The volume calibration has shown slight sensitivity to variable frame size and therefore steps should be taken to ensure the experimental video and calibration standards have the same ROI.

B.4.3 Temperature Save

The rate of temperature acquisition is set by the Order of Data Save control, which saves data at a rate of $10^x$ sec, where $x$ is the input value. To match to density, temperature data must be saved at the same rate or faster than the video data. A Frame Rate of 25 fps saves a frame every 40 ms, therefore the Order of Data Save must be $-1.4$ ($10^{-1.4} = 0.04$ sec) or less. The typical value of the Order of Data Save is -2 during measurements.

B.4.4 Calibration Standards

The camera settings (Exposure Time and Region of Interest) should be the same in the calibration video as it is in the experimental video for which the calibration standard is used. Frame Rate and Seconds of Video may be changed without loss of accuracy. The limiting factor for accuracy of a volume standard is the cleanliness of the samples. When dirty, the measured volume of the calibration standard oscillates (Appendix B.3.2). To detect this, Seconds of Video should be several times the period of sample rotation. The Frame Rate can be lowered to reduce the file size during the long data save. The standard settings for calibration standards are a Frame Rate of 10 fps and for Seconds of Video of 60 sec. At least two calibration standard measurements should be taken, in case the first standard is dirty. Optimally four standards, two before measurements and two after, should be measured to gauge variation in the position between samples.
B.5 References


Appendix C

X-ray Batch User’s Manual

C.1 Purpose

The X-ray Batch.vi software was created to improve the efficiency of the analysis of X-ray detector images acquired during Beamline Electrostatic Levitation (BESL) experiments. Prior to 2010, analysis of images acquired by during BESL experiments utilized the following programs: Origin® [1], ImageJ [2], Fit2D [3], PDFGetX2 [4] and a custom script for background subtraction [5]. X-ray Batch.vi was designed to incorporate the functionality of these programs into an easy to use LabVIEW™ [6] Graphical User Interface (GUI). During the development of the software, several additional corrections specific to the geometry encountered during levitation experiments were derived and reported [7, 8]. These corrections are discussed in Ch. 3 of this dissertation and were also incorporated into X-ray Batch.vi.

This manual was written to get a new user started on analyzing BESL data with X-ray Batch.vi. This is not intended to be a tutorial on general X-ray analysis; for details of the individual corrections see [8, 9]. For in-program help, use the LabVIEW™ context help window (Ctrl+H or Help → Show Context Help on the menu bar), or right click the
front panel object in question and select **Description and Tip**. The descriptions of each control were reprinted for the user’s reference in the *Glossary*.

### C.2 Manual Conventions

**Bold** - Bold text denotes controls and indicators in LabVIEW™ software.

*Italic* - Italic text denotes emphasis, names/labels, LabVIEW™ terminology, variables and options.

**Typewriter** - Typewriter text denoted paths and folder names.

### C.3 Installation

*X-ray Batch.vi* is part of the *BESL LabVIEW Analysis* package, which is a folder hierarchy that includes all software components and databases for LabVIEW™ analysis of BESL X-ray and thermophysical measurements. *X-ray Batch.vi* is found in the path *BESL LabVIEW Analysis/X-ray Analysis/X-ray Batch.vi*, and requires LabVIEW™ version 2012 or later.

### C.4 Basic Interface

The *X-ray Batch.vi* interface has three components, shown in Fig. C.1. The **Settings tab control** (1) contains the user supplied sample and correction information required for the
calculation and saving of X-ray analysis steps. The **Display tab control** (2) contains **pages** for each major step in the X-ray data reduction and analysis. Outside of the two containers is the **Progress Controls** (3), the set of controls and indicators for the progress through the X-ray file.

![Image](image_url)

**Figure C.1:** The *Front Panel* display of *X-ray Batch.vi* with the three main interface components circled: (1) the **Settings** tab control (2) the **Display** tab control and (3) the **Progress Controls**.

### C.5 Program Initialization

On clicking the run button located at the top left of the program, the program will start initialization. During initialization, *X-ray Batch.vi* will be load the X-ray file indicated in the **X-ray file Path** control on the **File Paths** page of the **Display** (Fig. C.2). If *X-ray*
file Path is empty, the user is prompted for the location of the X-ray file to analyze. The compatible files types are TIF files, PDS (PixeLINK™ Data Stream) files, mar detector files and GE Revolution™ detector files.

![Image of the File Paths page of the Display tab control.]

Figure C.2: The File Paths page of the Display tab control.

When an X-ray file is loaded into memory, the intensity of the pixels within each frame are averaged. The average intensity of each frame is scaled so that the frame with the highest average pixel intensity is given a value of one while the frame with lowest intensity is given a value of zero. This is graphed in the Normalized Frame Intensity plot on the Shutter page of the Display (Fig. C.3). When the X-ray file contains a combination of dark frames and measurement frames, the frame ranges of the measurements are identified in the Frames for Shutter On/Off indicator on the same page.

Next, the corrections settings are filled from the text file identified in the History Text File on the File Paths page. If no .txt file is entered, a two-button dialog will prompt the user
for the next course of action (Fig. C.4). The actions available are to click No, Cancel, which performs no action, or to click Yes, which will determine detector settings (i.e., the beam center, working distance and tilt) from a silicon standard calibration. If Yes is chosen, the user is prompted for the location of a silicon standard file. The user will also be prompted for a file containing the silicon standard’s background intensity, though this is not required for the silicon calibration.

A dialog subVI (ManualEstimateSi.vi, shown in Fig. C.5) will open showing the background subtracted silicon X-ray image. The purpose of this dialog is to allow the user to identify three coordinates located on the first ring of the silicon diffraction pattern. These coordinates are entered in the three Point on First Ring clusters and are highlighted in red on the Image Intensity Graph. With these coordinates, the Wavelength (Å) and Size of Pixels
(microns) (part of the Diffraction Parameters cluster) this program estimates the X-ray beam center and working distance for a detector perpendicular to the X-ray beam.

Figure C.4: The prompt for next action on failed loading of a history file.

Figure C.5: The front panel display for ManualEstimateSi.vi.
When three points have been identified, click the **OK** button to perform a least-squares refinement of the diffraction settings. A history `.txt` file will be created with the same name as the silicon X-ray file that can be loaded in future analysis. Clicking **Cancel** in either `ManualEstimateSi.vi` or the prompt for the silicon X-ray file location will result in no changes in `X-ray Batch.vi`.

When filled, the following files on the **File Paths page** of the **Display** will also load at run-time:

- **Empty Chamber Frames** - Specifies the file path and frames contained in the file to be averaged for an empty chamber image (dark plus background image).

- **Dark Frames** - Specifies the file path and frames contained in the file to be averaged for an image of dark signal from the detector.

- **Gain Map Path** - Specifies the file path of the manufacturer supplied detector gain map.

- **Bad Pixel Map Path** - Specifies the file path of a saved bad pixel map (`.mask` file).

Other settings used on initialization are also entered on the **File Paths page**. The **Frequency (Hz)** control located at the top of the **page** specifies the sampling rate of the X-ray acquisition file. This is used to determine the time stamp of each frame in the X-ray file. The **Width** and **Height** in the **Video Image Size cluster** indicates the dimensions of each frame in the detector file (automatically updated from header information when available). The **Bin Size of Raw Image** control resizes the detector image across both dimensions by the specified factor. This can be used to prevent the **memory overflow** error encountered when analyzing large detector images.
C.6  Program Operation

After initialization, X-ray Batch.vi proceeds through the calculations steps, shown above, for the X-ray image selected. The current step of calculation will be displayed in the Message string at the left of the Progress Controls.

For programmers wishing to modify X-ray Batch.vi, the block diagram execution is split into three state machines: (1) A producer loop, (2) a consumer loop and (3) a display loop. The producer loop responds to user changes to front panel objects by enqueueing (programmatically storing) actions to be performed by the consumer and/or the display loops. The consumer loop handles operations that are not necessary in every iteration of the analysis, such as loading and saving files. The display loop follows the execution flow of the analysis steps described here.
C.6.1 2D Indices

The first step in the analysis is the calculation of the solid angle coordinates and tilt encountered for each point on the X-ray image. The settings for these calculations are found on the Detector page of the Settings tab control. These settings are automatically updated when a silicon calibration standard is used.

C.6.2 I(q) 2D Corrections
Using the 2D Indices and the I(q) Inputs from the I(q) Settings page of the Settings (Fig. C.6) the corrections for polarization, oblique incidence and the geometric correction are calculated.

Figure C.6: The I(q) Inputs from the I(q) Settings page of the Settings tab control.

For the polarization correction, the Angle of Polarization (degrees) specifies the polarization plane, relative to the horizontal. The Polarization in-plane is the fraction of intensity parallel to the plane specified by the Angle of Polarization (e.g., Polarization in-plane = 0.5 for an unpolarized beam and 1.0 for a beam polarized in the plane specified by the Angle of Polarization).
The frames of the X-ray file for current analysis are identified in the progress controls, shown in Fig. C.7. The Progress Bar (frames) and Frames to Combine identify the beginning and number of frames, respectively, which are averaged for the current analysis. Clicking Progress through frames automatically increments the Progress Bar (frames) by the Frames to Combine at the end of the Wait to Proceed step in the analysis, restarting at this step.

Figure C.7: The Progress Controls.
After the average detector frame is loaded into memory, the dark and background images are subtracted. The dark image is the **Dark Frames** image loaded on initialization. The background image is the **Empty Chamber Frames** image loaded on initialization, minus the dark image. Before subtraction from the detector image, the dark and backgrounds images are scaled by the **Dark * and Background * (I(q) Settings page of Settings)** multipliers. In addition, the **Diffuse Background** (also on **I(q) Settings page**) is incorporated to mimic secondary fluorescence from the container not accounted for by the background. This is a flat subtraction across the entire detector image in detector units.

Following the background subtraction, the gain correction and the **I(q) 2D Corrections** are applied. To ease comparison between acquisition files, the detector is also multiplied by the **Frequency (Hz)** of the X-ray file.

### C.6.4 Update Time/Temp

![Diagram](image-url)
During BESL experiments, X-ray data is acquired during dynamic temperature control. If a temperature file is loaded, the temperature as a function time will be displayed on the Temp/Time page of the Display (Fig. C.8).

Figure C.8: The Temp/Time page of the Display tab control.

Using the time stamp in the X-ray file, the temperature time stamp, and the Frequency (Hz) input; the shutter and frame progress will be displayed on the same graph. Differences in system clocks between the temperature acquisition computer and the X-ray acquisition computer can be accounted for with the Time Difference (sec) control on the Temp/Time page.

The average temperature during each frame’s exposure is calculated and displayed on the Temp/Frame page of the Display. The average temperature of the current frame will appear in the Frame Temperature indicator below the Stop Program button. If no temperature file is loaded, the Frame Temperature is not displayed.
A temperature file is loaded by clicking the browse button next to the Temperature File path control. This opens a prompt for the temperature file path and opens EmCorrectTempData.vi. This vi, shown in Fig. C.9, is used to emissivity correct temperature data from the Washington University (WU-BESL) experiments. After emissivity correction, the data is loaded into X-ray Batch.vi for matching with detector data.

Figure C.9: The front panel display for EmCorrectTempData.vi.
C.6.5 Update Sample Info

Many of the corrections for X-ray data depend on the sample characteristics; in particular, composition, density, and linear attenuation (MuT). Composition and the temperature dependent Density are entered on Sample Settings page of the Settings (Fig. C.10).

The Density is entered in the form \( \rho = \rho_0 + d\rho/dT (T - T_0) \), where \( \rho_0 \) is the Density at \( T_0 \), and \( d\rho/dT \) is \( d\text{Rho}/dT \) at \( T_0 \). Using the Frame Temperature this is evaluated to calculate the Frame Density (displayed on G(r) Settings page). If no Frame Temperature is available, the Frame Density is set equal to the Density at \( T_0 \).

MuT is entered in the S(q) Correction Settings on the S(q) Settings page of the Settings. X-ray Batch.vi estimates the linear attenuation for spherical samples from the inputs on the Sample Settings page, the Frame Density and X-ray Wavelength (A). The results of this calculation are displayed at MuT Calculated on Sample Settings page. If the Density Correction button is ON, then the MuT control is changed to match MuT Calculated at this step in the analysis.
Figure C.10: The **Sample Settings** page of the **Settings** tab control.

### C.6.6 Solve Absorption Asymmetry

```
Calculate 2D Indices → Calculate I(q) 2D Corrections → Get Frame → Update Time/Temp → Update Sample Info

Calculate S(q) Corrections ← Angular Average to I(q) ← Update .COR ← Calculate 2D Spherical Corrections ← Solve Absorption Asymmetry

I(q) to S(q) ← S(q) to G(r), g(r) ← Minimize PDF Gauge ← Save ← Wait to Proceed
```

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For spherical samples, self absorption can create significant asymmetry in the measured intensity across the detector image. The degree of asymmetry in the detector can be viewed on the Detector Asymmetry page, within the I(q) page of the Display (Fig. C.11).

Figure C.11: The Detector Asymmetry page of the I(q) page of the Display tab control.

To limit unnecessary calculations, the Detector Asymmetry is only calculated when the Show Asymmetry button is ON. To prevent small pixel fluctuations from influencing the calculation, the detector asymmetry is averaged into bins of Smooth nxn pixels on each side. The toggle button above the Detector Asymmetry image sets whether the image displays asymmetry before spherical corrections (Raw) or after (Corrected). The asymmetry predicted by the spherical corrections with the current Composition, MuT, Ratio of Beam Offset to Sample Radius and Angle of Beam Offset to Center (rad) settings are shown in the 2D Spherical Corrections image.
If the Solve for Absorption Asymmetry button is ON at this step in the analysis, the Ratio of Beam Offset to Sample Radius and the Angle of Beam Offset to Center (rad) in the S(q) Correction Settings on the S(q) Settings page of the Settings are varied to minimize the Corrected Detector Asymmetry.

C.6.7 2D Spherical Corrections

Calculate 2D Indices → Calculate I(q) 2D Corrections → Get Frame → Update Time/Temperature → Update Sample Info

Calculate S(q) Corrections → Angular Average to I(q) → Update .COR → Calculate 2D Spherical Corrections → Solve Absorption Asymmetry

I(q) to S(q) → S(q) to G(r), g(r) → Minimize PDF Gauge → Save → Wait to Proceed

At this stage in the analysis, the 2-dimensional corrections (self absorption and/or multiple scattering) are calculated for each pixel in the detector file. These calculations are only performed for non-axial symmetric spherical geometries. The Geometry of the X-ray experiment is selected in the S(q) Correction Settings on the S(q) Settings page of the Settings. The Geometry Offset Spherical Absorption calculates only the absorption correction for an offset geometry. In this case, secondary scattering is approximated as the axially symmetric case for a more rapid computation. The Geometry Offset Spherical All calculates both 2-dimensional spherical absorption and secondary scattering corrections. These calculations are extremely CPU intensive and slow. The Progress Bar will appear below the Message string to indicate progress through these calculations.
The 2D Spherical Corrections are applied to the detector intensity calculated at the Get Frame step. The image is displayed on Frame Image page of the Display (Fig. C.12) with bad pixels set to a value of zero. A bad pixel map is loaded on initialization, if available, or be can created during analysis by clicking the Edit Bad Pixel Map button.

The Edit Bad Pixel Map button opens BadPixelMap.vi, shown in Fig. C.13. With BadPixelMap.vi, a bad pixel map may be loaded, saved and/or created. The Pixel Selection Options use entered variables to change pixels from good to bad, or vice versa. The cursor (left of the image) can be used help the user determine pixel coordinates. The Search for Bad Pixels and Crystals button identifies bad pixels by taking a normalized, numerical Laplacian at each pixel. Any pixel that has a normalized Laplacian outside a user-specifed number of standard deviations (Rejection Above X St Dev) from the average value is identified as bad pixel. Figure C.14 shows a diffraction pattern before and after bad pixels were identified and masked by the Search for Bad Pixels and Crystals function.
C.6.9 Angular Average to $I(q)$

After 2-dimensional corrections are applied to detector image, *X-ray Batch.vi* reduces the image to 1-dimensional data through an angular average. The angular averaged intensity is displayed on the $I(q)$ page in the $I(q)$ page of the Display. The data presented is evenly
Figure C.13: The *front panel* display for *BadPixelMap.vi*.

spaced in $q(1/A)$, where the spacing is determined by the $q$-range of the detector image and the **Number of Bins** in $I(q)$ control located on the $I(q)$ **Settings** page of the **Settings**.

The error in $I(q)$ is calculated as twice the standard error in the mean of each bin. For accurate error estimates, it is important to verify that detector asymmetries have been removed. This can be confirmed by viewing the intensity as a function of angle at a given $q$ value (**at** $q$ control), displayed on the $I(\phi)$ **page** the $I(q)$ **page** of the **Display**.
Figure C.14: A diffraction image before (left) and after (right) bad pixel masking.

C.6.10 $S(q)$ Corrections

Using the $S(q)$ Correction Settings on the $S(q)$ Settings page of the Settings and the Composition, the 1-dimensional corrections for converting measured detector intensity to $S(q)$ are calculated for each $q$ bin. These corrections are self absorption, multiple scattering, Compton scattering, Laue diffuse scattering and atomic scattering factor weighting.
The self absorption and multiple scattering corrections depend on the Geometry. The geometries supported for these calculations are *Reflection, Direct Transmission, Symmetric Transmission, Centered Spherical, Offset Spherical Absorption* and *Offset Spherical All*, shown schematically in Fig. C.15.

*Reflection, Direct Transmission* and *Symmetric Transmission* are traditional planar sample X-ray geometries. *Centered Spherical, Offset Spherical Absorption* and *Offset Spherical All* are all corrections for small-beam spherical samples. *Centered Spherical* assumes perfect, axially symmetric, alignment of X-rays with the sample. As noted earlier, *Offset Spherical Absorption* uses the axially symmetric approximation for multiple scattering corrections, but not for self absorption. In *Offset Spherical All*, both self absorption and multiple scattering corrections are 2-dimensional. It is important to note that although all absorption and secondary scattering corrections are supported for all of these geometries, the calculation of *2D Indices* is based on transmission. For full functionality in *Reflection* or *Symmetric Transmission* geometries, *X-ray Batch.vi* requires modification.
C.6.11 I(q) to S(q)

The settings for the conversion from I(q) to S(q) (displayed on the S(q) page of the Display) are entered in the S(q) Scaling Inputs on the S(q) Settings page of the Settings, shown in Fig. C.16.

First, the I(q) is cropped to a user specified range of useful data set by the Start/End control. The corrections to be applied to I(q) can be turned ON or OFF by clicking the relevant correction button in the Turn On/Off Corrections cluster. Only two of these corrections, Autoscale and Autoscale Fluorescence, are calculated at this step.

Autoscale and Autoscale Fluorescence corrections vary the Scale and/or the Fluorescence %Z^2 inputs to fix a physical behavior in S(q). The desired physical behavior is selected in the Autoscale Method radio selection. The High q Tail option induces S(q) to oscillate about one within the q range specified in the Autoscale Limits. The Low R Density option is an adaptation of the Krogh-Moe-Norman normalization, which sets the slope of G(r) equal to \(-4\pi\rho\) at \(r = 0\). The Low R Oscillations option attempts to minimize the ripples within the hard-sphere cut-off of G(r). The Low q Cut off is not used in the...
Figure C.16: The S(q) Scaling Inputs on the S(q) Settings page of the Settings tab control.

Low R Density and Low R Oscillation autoscale methods, however the High q Cut off sets the upper limit for the I(q) data used to perform the autoscaling. Autoscaling changes the Scale and/or the Fluorescence %Z^2 inputs, however, whether autoscaling is ON or OFF the values entered in the inputs are always used for the corrections. To disable the fluorescence correction, Autoscale Fluorescence must be OFF and Fluorescence %Z^2 must be set to zero.
C.6.12  S(q) to G(r), g(r)

The settings for the Fourier transform from the S(q) to G(r) are entered in the G(r) Inputs cluster on the G(r) Settings page of the Settings tab control, shown in Fig. C.17. The range and spacing in r for the calculation is set by the G(r) Grid control in the G(r) Inputs cluster. As a reference to the user, the spacing set by Nyquist-Shannon sampling theorem is displayed in the Nyquist Spacing (A) indicator. For a smoother G(r), damping functions can be applied to $q(S(q)-1)$. All damping functions are set to a value of one up to the $q_0 = \text{High X Start (X0)}$ after which they damp the function to zero at $q_{\text{max}}$. Supported damping functions, $D(q)$, are:

$Lorch - D(q) = \sin \left[ \pi (q_{\text{max}} - q_0) (q - q_0) \right] (q_{\text{max}} - q_0) / \pi (q - q_0)$

$Logarithm - D(q) = 1 - \log \left[ 10 (q - q_0 + 1) / (q_{\text{max}} - q_0 + 1) \right]$  

$Exponential - D(q) = \{ \exp [(q - q_0) / (q_{\text{max}} - q_0)] - e \} / (1 - e)$

$Cosine - D(q) = \cos \left[ \pi (q - q_0) / 2 (q_{\text{max}} - q_0) \right]$
$S(q)$ is updated to include the effects of the damping function for the user's reference (i.e., $S(q) = D(q)[S(q) - 1] + 1$).

Figure C.17: The $G(r)$ Settings page of the Settings tab control.

The $G(r)$ is displayed on the $G(r)$ page on the $G(r)/g(r)$ page of the Display. Uncertainties propagated from statistics and autoscale corrections in $S(q)$ can be displayed in $G(r)$ by clicking the relevant check boxes on the Show Uncertainty control. These errors are calculated to 95% confidence.
Using the **Frame Density**, \( G(r) \) is converted to \( g(r) \) and displayed on the \( g(r) \) page on the \( G(r)/g(r) \) page of the Display. For comparison with **Frame Density**, a linear fit of the low-\( r \) \( G(r) \) is used to estimate the density and is displayed in the **Estimated Density from \( G(r) \)** indicator. The slope of \( G(r) \) at the intercept, \( 2/\pi \int_{0}^{\infty} Q^2 [S(Q) - 1] dQ \), is also used to estimate the density, displayed in the **Estimated Density from \( S(q) \)**. The three densities displayed on the \( G(r) \) **Settings page** are \( XControls \), which allows them to toggle between number and mass density by clicking.

It is sometimes desirable to compare two \( G(r) \)'s through a difference curve. Clicking the **Hold for Difference** button on the \( G(r) \) page, stores the currently displayed \( G(r) \) on the Held \( G(r) \) graph on the **Held \( G(r) \)** page. When the calculations are updated and the \( G(r) \) changes, the difference between the Held \( G(r) \) and the current \( G(r) \) is displayed on the Difference Curve \( G(r) \) graph on the **Difference page**.

### C.6.13 Minimize PDF Gauge

```
Calculate 2D Indices  Calculate I(q) 2D Corrections  Get Frame  Update Time/Temp  Update Sample Info
Calculate S(q) Corrections  Angular Average to I(q)  Update .COR  Calculate 2D Spherical Corrections  Solve Absorption Asymmetry
I(q) to S(q)  S(q) to G(r), g(r)  Minimize PDF Gauge  Save  Wait to Proceed
```
A recently included feature to *X-ray Batch.vi* is the ability to automatically refine user inputs by a golden section minimization of the **PDF Gauge**. The **PDF Gauge** is a metric for low-\(r\) ripples; the same metric is minimized with the *Low R Oscillations* autoscaling method. The settings for this minimization are entered in the **Golden Section Search cluster** on the **G(r) Settings page** of the **Settings**. This refinement is currently available for **MuT**, **Background ***, **Dark *** and **Diffuse Background**, selected using the **Setting to Vary** drop down. A golden section search is performed within the bounds set by **Bounds (+/-)**, a value of 0.2 sets the bounds as plus/minus 20\% the initial value. The golden section search continues for the specified number of **Iterations**. Each iteration reduces the range of golden search by 62\%. To turn this feature ON, depress the **Minimize PDF Gauge** button. This minimization can be extremely time consuming, but can be interrupted at any time by unclicking the **Minimize PDF Gauge** button. A progress slide below the **Golden Section Search** indicates the progress through the desired number of iterations. **NOTE** for spherical samples: the **Solve for Absorption Asymmetry** should be ON when performing the minimization. When varying **MuT** the **Density Correction** button must be OFF.
The steps in the calculations can be saved into comma separated (.csv files) for further analysis in spreadsheet and/or graphing software. As shown in Fig. C.18, each major step in the analysis has a button associated with it on the Save Settings page of the Settings. The Save History File button creates a .txt file that can be used to load the current settings used in the X-ray Batch.vi. Clicking any of the save buttons will create a file containing X-ray data analyzed up to that step to the file location indicated by Save Folder. They are saved under the name of the X-ray file Path with the file extension modified reflect frames used in the analysis, the file type save (e.g., for a g(r) file the extension is .PDF) and the spreadsheet extension .csv. The Save Corrections button next to Save S(q) File indicates whether the S(q) corrections are also saved in S(q) File. For automated data saving, Save 1D Frame Analysis should be turned ON. This depresses the Save I(q) File, Save S(q) File, Save G(r) File, Save g(r) File and Save Difference File buttons so that any change in the analysis is reflected in the saved file.
The special save files contain important frame information about the data analyzed, however the data displayed on each graph and/or image can be saved separately by clicking the **Save Graph** button after selecting desired graph from the **Graph to Save** drop box. When saving **XYGraphs** to a spreadsheet by this method, the user will be prompted for the save path and file name. For **IntensityGraphs**, **IntensityMapToPicture.vi** will open (Fig. C.19), which allows for manipulation of the scaling and, ultimately, the export of the data to a JPEG, PNG or BMP.
Figure C.19: The front panel display for *IntensityMaptoPicture.vi*.

**C.6.15 Wait to Proceed**

- Calculate 2D Indices
- Calculate I(q)
- Get Frame
- Update Time/Temp
- Update Sample Info
- Calculate S(q)
- Angular Average to I(q)
- Update .COR
- Calculate 2D Spherical Corrections
- Solve Absorption Asymmetry
- I(q) to S(q)
- S(q) to G(r), g(r)
- Minimize PDF Gauge
- Save
- Wait to Proceed
When all calculation and actions have been performed for the selected frames, *X-ray Batch.vi* waits for changes on the front panel. When a change is detected the program restarts the analysis from the step pertaining to the change (e.g., a change in the **Mass (mg)** control will restart the analysis from the *Update Sample Info* step). If a change does not alter the inputs for a processor intensive calculation, that calculation will not be recomputed. For example, a change in the **Mass (mg)** control, with the **Density Correction** OFF, will not trigger a recalculation of the 2-dimensional absorption correction because the parameters that go into the calculation did not change.

As noted earlier, depressing the **Progress through frames** button will automatically increment the **Progress Bar (frames)** for the next set of calculations. This is registered as a change, and repeats the analysis for the new frames starting from the *Get Frame* step.

### C.7 Glossary

**Display** *TabControl*

**File Paths** *Page*

- **X-ray file Path** *Path* - The detector file containing diffraction images.
- **X-ray Video Type** *Enum* - The video file type identified by the file extension.
  
  The compatible file types are TIF files, PDS (PixeLINK Data Stream) files, mar detector files and GE Revolution detector files.
- **Frequency (Hz)** *Digital* - The sampling frequency of the X-ray detector.
- **Gain Map Path** *Path* - The file containing the detector gain map image.
- **Video Image Size** *Cluster*
Bin Size of Raw Image *Digital* - The number of pixels averaged across each dimension, to reduce image size.

**Size** *Cluster* - The dimensions of a 2D array or image.

**Width** *Digital* - The width of the image in pixels.

**Height** *Digital* - The height of the image in pixels.

**Bad Pixel Map Path** *Path* - The file containing the bad pixel map image (*.mask)*.

**History Text File** *Path* - The file containing the settings for this analysis. Either a text file, created by this program, or a silicon calibration file.

**Empty Chamber Frames** *Cluster* - The file and frames to be averaged for the empty chamber image.

**Frame Range** *Cluster*

**End Frame** *Digital*

**Start Frame** *Digital*

**File Path** *Path*

**Dark Frames** *Cluster* - The file and frames to be averaged for the dark detector image.

**Frame Range** *Cluster*

**End Frame** *Digital*

**Start Frame** *Digital*

**File Path** *Path*

**Shutter** *Page*

**Normalized Frame Intensity** *WaveformGraph* - The intensity of the frames normalized to the highest and lowest frame intensity. This graph is used for identifying the dark frames in an acquisition.
Frames for Shutter On/Off *Array* - An array of ranges where the program has identified measurements among dark frames. This identification does not work if every frame in the X-ray file contains diffraction data.

**Temp t0** *Digital* - The start time of the temperature file, in seconds, since the beginning of the day.

**Detector Timing** *Cluster* - The video start time and acquisition rate.

**Time Stamp** *AbsTime* - The time stamp taken from the video file.

**Seconds from Midnight** *Digital* - The start time of the video file in number of seconds since the beginning of the day.

**fps** *Digital* - The acquisition rate of the video in frames per second.

Temp/Time *Page*

**Temperature File** *Path* - The path to the temperature file during which the diffraction data was acquired. If the path is empty, no temperature analysis is performed.

**Time Difference (sec)** *Digital* - The time difference, in seconds, between the temperature acquisition computer and the detector acquisition computer.

**Shutter** *XYGraph* - The graph used to align the detector time stamp with the temperature and the frame signal.

Temp/Frame *Page*

**Temperature Matched to Frame** *XYGraph* - A graph of the average temperature at each frame in the X-ray file.

Frame Image *Page*
**Image .COR** IntensityGraph - The detector image after background subtraction and all 2-dimensional corrections. Bad pixel points are set to an intensity of zero.

**Edit Bad Pixel Map** Boolean - Click to edit the Bad Pixel Map.

**I(q) Page**

**I(q) Graphs** TabControl

**I(q) Page**

**I(q) XYGraph** - A graph of the angular averaged intensity calculated from the diffraction data.

**I(\phi) Page**

**I(\phi) XYGraph** - A graph of the intensity as function of the polar coordinate (\phi) at the specified momentum transfer (q).

at q Digital - The q-bin displayed in the I(\phi) graph.

**Detector Asymmetry** Page

**2D Spherical Corrections** IntensityGraph - The absorption and secondary scattering corrections applied to the detector due to off-axis spherical transmission. When ‘Show Asymmetry’ is ON the correction at each pixel is divided by the angular averaged correction.

**Solve for Absorption Asymmetry** Boolean - Click ON to solve for the beam incidence on a spherical sample, relative to the sample’s central axis, by minimization of the detector asymmetry.

**Show Asymmetry** Boolean - Click ON to calculate the asymmetry in the spherical correction, displayed in the ‘2D Spherical Corrections’ graph, and the asymmetry in the detector, displayed in the ‘Detector
Asymmetry’ graph. The asymmetry is calculated by the value at each pixel divided by the angular averaged value.

**Detector Asymmetry IntensityGraph** - A display of the detector value at each pixel divided by the angular averaged value. This is only calculated when ‘Show Asymmetry’ is ON.

**Detector Asymmetry Boolean** - Click to toggle between ‘Raw’ and ‘Corrected’, which displays ‘Detector Asymmetry’ before and after spherical corrections, respectively.

**Smooth nxn Digital** - Smooths the ‘Detector Asymmetry’ by the factor specified.

**S(q) Page**

**S(q) XYGraph** - A graph of the structure function (sometimes called the structure factor) calculated from the diffraction data.

**G(r)/g(r) Page**

**Real Space Graphs TabControl**

**G(r) Page**

**G(r) XYGraph** - A graph of the reduced pair distribution function (RPDF) calculated from the diffraction data.

**Hold for Difference Boolean** - Click to hold the current G(r) for difference comparison with future G(r)s.

**g(r) Page**

**g(r) XYGraph** - A graph of the pair distribution function (PDF) calculated from the diffraction data.

**Difference Page**
Difference Curve $G(r)$ \textit{XYGraph} - A graph of the difference between the current $G(r)$ and held $G(r)$.

Held Temperature \textit{Digital} - The temperature of the $G(r)$ subtracted off from the current $G(r)$ for the difference curve.

Held $G(r)$ \textit{Page}

Held $G(r)$ \textit{XYGraph} - A graph of the $G(r)$ held for difference comparison.

\textbf{Settings} \textit{TabControl}

\textbf{Detector} \textit{Page}

\textbf{Diffraction Parameters} \textit{Cluster} - These parameters are dependent on the detector and geometry of the experimental set-up. They are used to convert pixel coordinates to q-space coordinates.

\textbf{Tilt Angle (degrees)} \textit{Digital} - The angle by which the detector is rotated (tilted) toward the sample. (NOTE: This tilt angle is negative relative to the output of Fit2D).

\textbf{Tilt Axis (degrees)} \textit{Digital} - The axis along which the detector is rotated (tilted) toward the sample.

\textbf{Working Distance (mm)} \textit{Digital} - The distance from the sample to the detector in millimeters.

\textbf{Size of Pixels (microns)} \textit{Digital} - The length of one side of a square pixel on the detector in micrometers.

\textbf{Wavelength (Å)} \textit{Digital} - The wavelength of the incident beam in Angstroms.

\textbf{Center Y} \textit{Digital} - The beam center on the detector along the vertical in pixels.
Center X  *Digital* - The beam center on the detector along the horizontal in pixels.

**Sample Settings Page**

**Composition Cluster** - A list of the sample composition using element abbreviations and atomic percent.

**Composition Weighting Array** - A list of the atomic percent of each constituent element in the accompanying array. If the sum does not equal 100%, the weighting is divided by the total (e.g. [3,5]=[3/8,5/8]). Delete extra space by Right click+Data Operations+Delete Element.

**Elements Array** - A list of the sample constituent elements (abbreviations). Delete extra space by Right click+Data Operations+Delete Element.

**Mass (mg) Digital** - The mass of the sample in milligrams, used to estimate MuT when the ‘Density Correction’ is applied.

**Density Cluster** - The density settings used for calculating g(r) and MuT.

**dRho/dT at T0 Digital** - The slope of the density with respect to temperature at T0. When temperature data is unavailable, this is ignored.

**T0 (C) Digital** - The reference temperature, in Celsius, about which the density linear fit was calculated.

**Density at T0 Digital** - The density, in grams per cubic centimeter, at the reference temperature, T0. When temperature data is unavailable this is the density used.

**Density Correction Boolean** - Click ON to automatically update the linear attenuation of the sample (MuT) upon changes in the sample density. A spherical sample is assumed.
MuT Calculated Digital - The estimated MuT based on the sample composition and the frame density. MuT is the attenuation coefficient of the sample (Mu) multiplied by the sample thickness (T). The sample is assumed to be spherical (T=2r) for the calculation of the thickness.

Sample Info Cluster - The properties of the sample estimated from the compositional information.

⟨Z²⟩ Digital - The square average atomic number.

⟨Z⟩ Digital - The average atomic number.

Molar Mass Digital - The molar mass of the sample.

Ideal Density Estimate Digital - The density of the sample estimated from the weighted average specific volumes of the constituent elements.

Mu/Rho Digital - The linear attenuation coefficient (Mu) divided by density (Rho).

I(q) Settings Page

I(q) Inputs Cluster - Settings for 2D corrections applied to detector image before taking the integral average about azimuthal angle to get I(q).

Transmission through Detector Digital - An estimate of the percent transmission through the detector for an X-ray at perpendicular incidence. This is used to correct for the extra length a diffracted photon must travel in the detector at high angles compared to normal incidence.

Geometric Correction Boolean - Click ON to enable the flux normalization. This converts the intensity measured at each pixel to the flux of the corresponding solid angle.
**Angle of Polarization** *Digital* - The angle of polarization which defines the axis of horizontal polarization.

**Polarization in-plane** *Digital* - The percent of the intensity horizontally polarized (zero, vertically polarized).

**Dark** *Digital* - The multiplier on the dark intensity before subtraction from the detector image.

**Background** *Digital* - The multiplier on the background intensity (Empty Chamber-Dark) before subtraction from the detector image.

**Diffuse Background** *Digital* - A constant subtraction, in detector units, across the entire detector image.

**Number of Bins in I(q)** *Digital* - The number of bins, in q, to be used in the rebinning of the angular average for evenly spaced I(q) and S(q) data.

**S(q) Settings** *Page*

**S(q) Correction Settings** *Cluster*

**Angle of Beam Offset to Center (rad)** *Digital* - The angle from the horizontal to the center of the sample, when looking down the beam path. Used only for ‘Offset Spherical’ geometries.

**Ratio of Beam Offset to Sample Radius** *Digital* - The distance from the beam axis to the central axis of a spherical sample in units of the sample radius. Used only for ‘Offset Spherical’ geometries.

**Recoil Exponent** *Digital* - This is the exponent for the Breit-Dirac recoil factor. This should have a value of two for counting detectors and three for intensity detectors.
**MuT Digital** - The attenuation coefficient of the sample (Mu) multiplied by the sample thickness (T). For spherical samples, use the sample diameter (T=2r) for the thickness.

**Geometry Enum** - The experimental geometry of the diffraction measurement. ‘Reflection’, ‘Direct Transmission’ and ‘Symmetric Transmission’ are used for planar samples. For an X-ray beam passing through a planar sample to a plate detector use ‘Direct Transmission’. For BESL experiments, use one of the spherical geometries. The ‘Centered Spherical’ geometry assumes the beam is perfectly aligned to the center of the sample. ‘Offset Spherical Absorption’ takes into account off-axis transmission for absorption calculation, but not for secondary scattering. ‘Offset Spherical All’ calculates the off-axis corrections for both absorption and secondary scattering.

**S(q) Scaling Inputs Cluster**

**Autoscale Method RadioButtonsControl** - The method used to autoscale corrections. ‘High q Tail’ attempts to cause the S(q) to oscillate around one within the ‘Autoscale Limits’. ‘Low R Density’ scales S(q) so that the density determined by the slope of G(r) at low-r matches the experimental density (also called Krogh-Moe-Norman normalization). ‘Low R Oscillations’ scales S(q) to minimize the ‘PDF Gauge’.

**Fluorescence %Z^2 Digital** - The approximate percentage of the signal due to fluorescence.

**Scale Digital** - The intensity normalization used to convert detector units to electron units.
**Autoscale Limits** *Cluster* - The autoscale limits identifies the range of $S(q)$ used for the autoscale methods. For the ‘High q Tail’ methods, this defines the range of data the user wants to oscillate about one. For the ‘Low R Density’ and ‘Low R Oscillations’ methods, the high bound of the data used for autoscaling is the minimum of the ‘High q Cut off’ and ‘Start/End High q’.

**Low q Cut off** *Digital*

**High q Cut off** *Digital*

**Start/End** *Cluster* - The range in $q$ for the $S(q)$ to be considered.

**Low q** *Digital*

**High q** *Digital*

**Turn On/Off Corrections** *Cluster* - Click ON (Bright Green) to enable each correction.

**Autoscale** *Boolean* - The automatic determination of the scaling parameter that converts detector intensity to electron units.

**⟨asf⟩^2 Weighting** *Boolean* - The scaling of the coherent scattering cross-section by the average atomic form factor ($asf$) squared. This is part of the definition of the structure function.

**Laue Diffuse Scattering** *Boolean* - The subtraction of the monotonic cross-section ($⟨asf^2⟩-⟨asf⟩^2$).

**Compton Scattering** *Boolean* - The correction for incoherent scattering in the sample.

**Autoscale Fluorescence** *Boolean* - The automatic determination of the fluorescence correction, a flat subtraction across all solid angles.
Multiple Scattering  Boolean - The correction for secondary scattering of the diffraction beam by the sample.

Self Absorption  Boolean - The correction for absorption of the diffraction beam by the sample.

G(r) Settings  Page

G(r) Inputs  Cluster - The inputs for the Fourier transform of S(q) to G(r).

Apply Damping  Cluster

High X Start (X0)  Digital - The value in q to begin the damping function. Below this value the S(q) is unaffected.

Damping Function  Enum - The function to be applied to q(S(q)-1) to smooth G(r).

Show Uncertainty  Cluster - Select the uncertainties to be displayed with the G(r).

Correction  Boolean - Click to show the uncertainty due to uncertainties in autoscaling.

Statistical  Boolean - Click to show the uncertainty due to statistical uncertainty in S(q).

G(r) Grid  Cluster - The range over which to calculate G(r).

Low r  Digital - The lower bound of the G(r) grid.

Spacing  Digital - The spacing between points on the G(r) grid.

High r  Digital - The upper bound of the G(r) grid.

Nyquist Spacing (A)  Digital - The spacing dictated by the Nyquist-Shannon Theorem, “If a function x(t) contains no frequencies higher than B hertz, it
is completely determined by giving its coordinates at a series of points spaced 1/(2B) seconds apart."

**Frame Density** *XControl Density* - The density utilized for the analysis.

**Estimated Density from G(r)** *XControl Density* - The density calculated from the slope of G(r) in the hard sphere limit, G(r)=-4*Pi*r*rho0 for r < (r cut-off).

**Estimated Density from S(q)** *XControl Density* - The density calculated from the slope of G(r) at r=0, Rho0=int(Qˆ2*(S(Q)-1),Q=0..infinity)/(-2*Piˆ2).

**PDF Gauge** *Digital* - A gauge that quantifies the quality of the data by the magnitude of the ripples at low-r (see [10]).

**Golden Section Search** *Cluster*

  **Iterations** *Digital* - The number of iterations to perform the golden section search. Each iteration reduces the bounds by 62%.

  **Bounds** (+/-) *Digital* - The bounds of the golden section search, in fraction of initial value (e.g., a value of 0.2 indicates the bounds are plus/minus 20% the initial value).

  **Minimize PDF Gauge** *Boolean* - Click ON to minimize the low-r ripples using a golden section search on the selected parameter.

  **Setting to Vary** *Enum* - The setting varied to minimize the PDF gauge. Possible options are ‘Background *’, ‘Dark *’, ‘Diffuse Background’ and ‘MuT’.

  **Minimization Progress** *Slide* - The progress through the iterations of the golden section minimization.

**Save Settings** *Page*
Save Folder  Path - The save destination folder. By default this is the X-ray file location.

Save History File  Boolean - Click to save a text file which can used to load settings in future analysis.

Save .COR File  Boolean - Click to save the detector image, after background and dark subtraction. Used for analysis in Fit2D (*.sum.cor).

Save I(q) File  Boolean - Click to save the I(q) data to a spreadsheet file (*.I.csv).

Save S(q) File  Boolean - Click to save the S(q) data to a spreadsheet file. If ‘Save Correction’ is ON, all conversion factors from I(q) are included in the file (*.S.csv).

Save Corrections  Boolean - Click ON (Bright Red) to include the corrections from I(q) to S(q) to be saved with S(q) files.

Save G(r) File  Boolean - Click to save the G(r) to a spreadsheet file (*.G.csv).

Save g(r) File  Boolean - Click to save the g(r) to a spreadsheet file (*.PDF.csv).

Save Difference File  Boolean - Click to save G(r) difference to a spreadsheet file (*.DG.csv).

Save 1D Frame Analysis  Boolean - Click ON to save the I(q), the S(q), the G(r), the g(r) and the Difference files with each iteration of the analysis.

Save Graph  Boolean - Click to save the data from the identified graph to a spreadsheet file.

Graph to Save  Enum - The graph saved when Save Graph is clicked.

Progress Controls  TabControl

Progress Controls  Page
Progress through frames **Boolean** - Click PLAY to add the number of averaged frames to the progress bar at the end of the calculation steps. Click PAUSE to stop automatic progression.

Stop Program **Boolean** - Click to stop program execution. The current calculation will be aborted.

Progress Bar (frames) **Slide** - The index of the beginning frame for the current analysis.

Frames to Combine **Digital** - The number of frames averaged for the current analysis.

Elapsed Time (sec) **Digital** - The estimate of the elapsed time from the beginning of the X-ray file to the progress bar frame. This is calculated from the sampling frequency of the detector.

Frame Temperature **Digital** - The average temperature of the current frames.

Message **String** - A descriptor of the program execution.

Progress Bar **Slide** - The progress of the current analysis step.

C.8 References


