THE STRUCTURE AND DYNAMICS OF MONATOMIC LIQUID POLYMORPHS

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Adam	n Cadien
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1	of
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L	
Committee:	
	Dr. Howard Sheng,
	Dissertation Director
	Dr. Dimitrios Papaconstantopoulos
	Committee Member
	Committee Member
	Dr. Estela Blaisten-Barojas.
	Committee Member
	Dr. Amarda Shehu,
	Committee Member
	Dr. Maria Dworzocka
	Dopartment Chair
	Department Chan
	Dr. Donna M. Fox.
	Associate Dean Office of Student Affairs &
	Special Programs College of Science
	Special Programs, conege of Science
	Dr. Peggy Agouris,
	Dean, College of Science
	, 0
Date:	Spring Semester 2015
	George Mason University
	Fairfax, VA

The Structure and Dynamics of Monatomic Liquid Polymorphs; Case Studies in Cerium and Germanium

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at George Mason University

By

Adam Cadien Master of Computational Materials Science George Mason University, 2012 Bachelor of Science University of British Columbia, 2008

Director: Dr. Howard Sheng, Professor Department of School of Physics, Astronomy, and Computational Sciences

> Spring Semester 2015 George Mason University Fairfax, VA

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Dedication

To Sarah, the love my life without whom I would have faltered. I owe her everything.

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List of Abbreviations

Abbreviation	Meaning
CRN	Continuous Random Network
DAC	Diamond Anvil Cell
DFT	Density Functional Theory
EAM	Embedded Atom Method
ELF	Electron Localization Function
FCC	Face Centered Cubic
GGA	Generalized Gradient Approximation
HDA	High Density Amorphous
HDL	High Density Liquid
HULDA	Hyper-Uniform Low Density Amorphous
ISF	Intermediate Scattering Function
KWW	Kohlrausch-Williams-Watts
LDA	Low Density Amorphous
LDL	Low Density Liquid
LLPT	Liquid-Liquid Phase Transition
MSD	Mean Square Displacement
NHN	Nearly Hyperuniform Network
PAW	Plane Augmented Wave
PBE	Perdew, Burke, Ernzerhof
PEL	Potential Energy Landscape
RDF	Radial Distribution Function
RMSD	Root-Mean Square Displacement
TOP	Tetrahedral Order Parameter
WRMSD	Windowed Root-Mean Square Displacement
WWW	Wooten-Winer-Weaire

Abstract

THE STRUCTURE AND DYNAMICS OF MONATOMIC LIQUID POLYMORPHS; CASE STUDIES IN CERIUM AND GERMANIUM

Adam Cadien, PhD

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Dissertation Director: Dr. Howard Sheng

The study of liquid polymorphism is at the frontier of fundamental thermodynamics and materials science. Liquid polymorphism occurs when a single material has multiple structurally unique liquid phases. Water was the first substance suggested to exhibit multiple liquid phases, a number of monatomic semiconductors and metals have been found to exhibit similar characteristics since then. A better understanding of the liquid-liquid phase transition is needed to tackle problems in glass sciences, it is also relevant to geophysical studies of the Earth's core and mantle and has applications in nanotechnology.

Computational methods are critical to developing a better understanding of liquids. Through simulation thermodynamic obstacles that hamper experiments can be artificially bypassed, metastable regions outside the equilibrium phase diagram can be accessed and all of the properties of the system are directly recorded. Computationally it is much simpler to iterate over a range of environmental variables such as temperature, pressure and composition, and measure a system's response. In this thesis *ab-initio* and semi-empirical approximations are used to accurately describe the complex many body interactions that take place in liquids.

Two independent case studies of liquid polymorphism are presented here. The first is a stable liquid-liquid phase transition was found to occur in Cerium which was initially discovered through X-Ray diffraction experiments and later confirmed through simulation. This phase transition is predicted to end at a critical point.

The second is a comprehensive study of the structure and dynamics of Germanium's many metastable amorphous and liquid phases. This is currently the largest *ab-initio* based study of the dynamics of Germanium's metastable liquid phases. Methods ranging from the mean square displacement to the van Hove function and intermediate scattering function are introduced and analyzed. The micro-structural characteristics are quantified and correlated with the mobility in the material revealing dynamical heterogeneity.

Chapter 1: Introduction

Of the three fundamental states of matter (gas, liquid, solid), liquid is the least understood. The study of solids follows directly from experiments which reveal their underlying structural characteristics; symmetry, basis vectors and composition. While both gases and liquids lack symmetry and periodicity, gases interact intermittently and interactions are often accurately described as weakly interacting soft spheres [11]. Liquids exist at a much higher density so they undergo constant and dynamic many-body interactions and are capable of exhibiting more complex behavior [12].

Simulation is a crucial and necessary method for advancing the understanding of liquids [13]. Through simulation thermodynamic obstacles that hamper experiments can be artificially bypassed, metastable regions outside the equilibrium phase diagram can be accessed and all of the properties of the system are recorded directly. Computationally it is much simpler to iterate over a range of environmental variables such as temperature, pressure and composition, and measure the system's response. Of course simulation based studies are not without challenges and deficiencies. The Potential Energy Landscape (PEL) [14, 15] that describes many body interactions, when studied through simulations is an approximation to that of empirical systems. So it is always necessary to test the accuracy of simulation methods, to enhance them with experimental data whenever possible and to verify that phenomenon observed in simulation are not artifacts of the selected approximations.

Polymorphism is a common phenomenon in solids, where a constant composition is maintained but various symmetries are exhibited. A similar incident can occur in liquids that exhibit short range symmetries [16], it has remained largely unstudied until recently when computational methods have increased in power and accuracy. Liquid polymorphism and the Liquid-Liquid Phase Transition (LLPT) are phenomena that are generally much easier to observe and probe through simulation than by experiment. Water was the first substance suggested to exhibit liquid polymorphism in both experiment [17, 18] and simulation [16]. A better understanding of the LLPT is needed to tackle problems in glass sciences [16, 19], better understanding water [18], it is also relevant to geophysical studies of Earth's core and mantle [20] and has applications in nanotechnology [21]. Liquid polymorphism is at the frontier of fundamental thermodynamics and materials science.

1.1 The Study of Liquids

The first rigorous attempt at constructing a formal framework for the study of disordered structures was by Bernal in 1959 [22]. Bernal generated randomly packed structures by filling balloons with plastic spheres. He then analysed these structures by counting the average number of neighbors and breaking down the structure through Voronoi tessellation to construct neighborhood polyhedra. Bernal's hard sphere arrangements demonstrated that densely packed random structures were predominantly composed of polyhedra with 5 sided faces [1]. The method of using Voronoi polyhedra was widely criticized due its static nature but is still used in the study of glassy and highly viscous amorphous structures today.

The study of liquids has matured since then and a number of experimental methods have since been developed that are capable of probing macroscopic properties. X-Ray diffraction can be used for studying bulk liquid structure *in-situ* at equilibrium and at fixed pressure and temperature [23]. Similarly the elastic properties of liquids can be probed through neutron scattering experiments. Thermodynamic properties like pressure, density, temperature and heat can be controlled for or measured accurately. The transport properties of liquids are studied through viscosity, self-diffusion, and a plethora of flow experiments.

A tremendous hurdle for experimentalists has been the question of how to achieve atomic scale resolution of a dynamic structure like a liquid. Transmission Electron Microscopy for example is capable of probing the structure of a few atomic surface layers, but this is only works for stable arrested structures. Also surfaces tend to distort the structure



Figure 1.1: (a) The 2D tessellation of liquids as presented by Bernal [1] and a 3D Voronoi tessellation of a simulated liquid.

of metastable phases or materials that are not strongly bonded. Macroscopic properties measured through experiment are essential to liquid study, they provide anchor points through which we can argue the validity of simulations. The study of microscopic liquid structure and dynamics are currently best studied through simulation and compared against the macroscopic measurements taken from experiment.

1.1.1 Negative Melting Curves

Macroscopic properties often demonstrate anomalous behavior which can then be probed through simulation. For example the well known volume expansion of water upon freezing which is demonstrated simply by freezing a plastic water bottle. This phenomenon coincides with a drop in density which is also plainly visible every winter when a body of water freezes and the ice floats on top. To the everyday observer this anomaly is so ubiquitous that they do not realize how truly bizarre it is.

To understand how counter intuitive this phenomenon really is let us consider a simple prototypical material, Copper. In its solid form Copper is stable in a crystal lattice. When heated the material expands as the atoms locked in lattice points begin to vibrate and contribute to the internal pressure. These vibrations grow as the temperature increases and force the material to expand as a result. As the temperature increases further the atomic vibrations expand beyond neighboring interstitial points and atoms begin to pop out of their stable lattice sites in the process known as melting. As the copper melts it transitions from a highly ordered crystal state to a disordered and dynamic liquid state. Atoms in a liquid move around much more than those in a solid and to account for this motion the volume of the copper increases as it melts as does its entropy. The entropy is a measure of how the energy is distributed across the states accessible to a material at a particular temperature, and is inversely correlated with the order present in the structure. From this information we can fill in one side of the Clausius-Clayperon equation which is defined for materials undergoing a phase transition;

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} \tag{1.1}$$

where dP/dT is the slope of the pressure temperature curve. The Δs and Δv are the change in entropy and change in volume associated with this phase transition. Both quantities in the right hand side of this equation are positive and as we know from the experimentally measured phase diagram, Copper does have a positive slope in dP/dT. This is true for most materials, they expand and experience an increase in entropy as they melt so we find a positive slope in the dP/dT of the melting curve.

Water and many other network forming liquids such as Germanium and Silicon as well as Cerium have negative melting curves. The change in entropy is positive for the process of melting [24] this implies that Δv will be negative so the right and left hand side of equation 1.1.1 are both negative. The net result of this is that the liquid phase is more dense than its solid counterpart which is counter to what seems clear from the Copper example.

The decrease of volume that occurs in these materials is justified by the existence of multiple liquid phases, each one corresponding to a solid counter part that it shares properties like density and conductivity with. It has been proposed that when a solid contracts upon melting it is not melting into its corresponding liquid phase [25].

1.1.2 Liquid-Liquid Phase Transitions

The negative melting curve is an indicator of multiple liquid phases. In many cases when a solid-liquid transition has a negative melting curve the solid will not share many characteristics with the liquid. Certainly there is a discontinuity in the density. For semiconductors Germanium and Silicon the high density liquid is metallic in nature while the low density crystal is semiconducting. On the other hand the high density liquid does share many characteracteristics with another crystal phase of the material which leads to the question of whether the stable solid phase has its own unique liquid counterpart. A second liquid phase with its own unique macroscopic properties which differentiates it from the stable liquid phase would exist either at high pressures or as a metastable phase [25, 26].



Figure 1.2: Schematic diagrams for liquid polymorphism. LDL is a low density liquid, HDL is high density liquid and VHDL is very high density liquid. Metastable phases are indicated by *.

For both of the cases in which a second liquid phase exists at extreme pressures or as a metastable phase, are difficult to probe in experiment. Some advances have occurred recently which makes this possible, for example advances in sealed Diamond Anvil Cell technology which encapsulate a sample and allow for simultaneous heating and pressurization enabled the X-Ray diffraction study in chapter 2. Further justification of this theory is taken from the concept of the PEL which can be directly probed in simulation.

1.1.3 The Potential Energy Landscape Connection

The potential energy landscape is a concept useful when discussing metastable states and supercooled liquids. To derive it we first consider a system of two atoms where the only relevant degrees of freedom are the coordinates of the atomic centers. The potential energy of this toy system is

$$V_2 = V(\vec{r}_1, \vec{r}_2) \tag{1.2}$$

where $\vec{r_i}$ is the coordinate vector of atom i. This can be simplified by considering only the distance between the atomic centers:

$$V_2 = V(\vec{r}_{12}) \tag{1.3}$$

where \vec{r}_{ij} is the distance vector between centers of atoms i and j. The complete definition of the potential energy will be discussed later. For a system of N atoms interacting through a pair potential we can define the potential energy as

$$V_N = \sum_{i=0}^{N-1} \sum_{j=i+1}^{N-1} V(\vec{r}_{ij}).$$
(1.4)

Higher order interactions (3-body, 4-body etc.) can also be included, but the potential energy is always a function of the 3N coordinate variables. This function can quickly become very large and impossible to visualize as bulk systems are on the order of Avagadro's Number in size. The PEL is the conceptual hypersurface defined by this complete potential energy function. To simplify this concept the PEL is typically visualized as a function of

one or two collective variables which serve as a reduction of variables. This is equivalent to cutting through the full hypersurface with a manifold of 1 or 2 dimensions. In figure 1.3 a simplified projection of the PEL with many local minima that represent metastable states and one global minimum that represents the ground state is considered.



Figure 1.3: A generic PEL. High temperature liquids exist well above the surface of the PEL, not persisting in any one state for much time. (1,2) Amorphous states lay closer to ther surface and exist only in broad local minima. (3,4) Crystalline phases are sharp steep wells, the ground state is the deepest of these (3).

Highly ordered, low energy crystalline states are deep narrow pits in the landscapes. The extreme depth of these pits is due to the high stability associated with crystalline states and the lack of stable neighboring states. Deformed states are broader and have multiple local minima surrounding them. The vast majority of the PEL encompassing all possible states of N atoms is unstable or metastable. There are some states that are not crystalline but have low energy. These highly disordered states belong to broad basins with many local minima and no well defined global minima.

All of the states on the surface of this landscape have no kinetic energy and are at 0 temperature. By adding in the kinetic degrees of freedom (force on each particle) we can access states that lie above the surface of the landscape. A system in the deep minimum of a crystalline phase will melt when enough kinetic energy is added to raise the system above the crystalline energy barrier.

1.2 Simulation Methods

The potential energy function used to describe the atomic system determines the shape of the PEL. A typical first principles approach starts by defining the Hamiltonian of the system and then uses the time dependent Schrödinger equation to propagate it [27]. However the complexity of systems with more than just a handful of electrons makes this method prohibitively expensive to use. One possible solution is to employ Density Functional Theory (DFT) and approximate the total Hamiltonian as interactions between electrons and electrons, between nuclei and electrons and between nuclei and nuclei. Using DFT it is possible to calculate the total energy of many systems of up to two to three hundred atoms. The DFT PEL is not the same shape as its real counterpart since it is an approximation to the full first principles Hamiltonian. This is akin to draping a sheet over a chair, the general shape of the chair is preserved but some of the finer detail is lost. DFT correctly predicts many bulk properties of materials and is sufficient to accurately describe the empirical PEL of many systems.

Simulating disordered structures requires a larger number of atoms relative to ordered crystalline structures. This is because of the disordered systems do not have the long scale symmetry that makes periodic boundary conditions advantageous for crystalline systems. Furthermore in a sufficiently small simulation box an atom can interact with itself through the periodic boundary causing artificial correlation effects. Spatial correlations (e.g. MSD, viscosity, auto-correlation) cannot be accurately measured with small simulation bounds. Model potentials were developed to speed up and avoid DFT's poor scaling properties and to better study more dynamic systems. These potentials are analytical models built to replicate macroscopic properties. Duplicating these properties relies upon a complex fitting process, minimizing the error between a set of empirical properties and values generated by the potential itself. A detailed description of the fitting process is given in Appendix B.

DFT has the advantage that it is an ab-initio method, meaning from the ground up, and does not rely on fitting to empirical data. In many ways this makes it the computational equivalent of experiment. This is in stark contrast to model potentials which rely on experimental data to fit to. Using most model simulation methods one can interpolate between experimental results but cannot effectively extrapolate to unexplored regions. Despite the computational challenges imposed on DFT based studies, it is necessary to apply these methods when studying disordered materials with complex electronic properties.

The study of liquids is often approached through the use of analytical or model interatomic potentials. These methods are useful because they are computationally efficient and straightforward to use and they allow for an enhanced sampling of murky phenomena. However when a potential is applied for an inappropriate application it is possible that it will generate artifacts that can be misleading. For example a ground breaking study by Glosli and Ree [28] found Carbon consisted of two stable liquid phases over a large temperature range, however the study used a model potential which was found to contain artificial properties. The finding was later refuted by a study from the same authors which used DFT simulations and showed no such transition occured [29]. This example highlights the necessity of accurate methods in studying metastable phases. The Stillinger-Weber potential [30] is a popular potential for studying both Silicon and Germanium systems, however it has been shown that by slightly toying with the angular contribution coefficient λ , it is possible to greatly affect the properties of the simulated liquid phases. Choosing an appropriate λ coefficient both extremely difficult and arbitrary as there are little experimental data to confirm the coefficient has been chosen properly.

For these reasons the DFT method was chosen for the study of Germanium and for the basis of the computational study of Cerium. This is the first such study of Germanium and largest study of its kind for any semiconductor as applied to the study of metastable liquid phases. Using highly accurate ab-initio molecular dynamics method a comprehensive study of the thermodynamics, static structure and dynamics of Germanium is generated.

1.3 Overview

In this work two independent studies of monatomic LLPT will be discussed and contrasted. In Chapter 2 a novel study of the lanthanide Cerium is studied via X-Ray diffraction. A new analysis method is developed and applied to extract relevant information from the experimental data in order to study the liquid phase of Cerium. Two stable liquids are found and analysed using through semi-empirical and DFT based simulation methods. Two model potentials are developed to study the static structure of the liquid phases seen in experiment as well as to calculate the free energy of the phases.

In Chapter 3 the semiconductor Germanium is introduced and a variety of simulation methods are applied to study the static characteristics of its metastable liquid and amorphous phases. The transition between static amorphous phases as a function of pressure is studied and an efficient method for observing this transition is developed. Computational geometry is applied to study the local structures that can describe and differentiate the amorphous structures. A shift from a highly defected glassy state to a hyperuniform one is investigated and studied using the long wavelength limit of the structure factor. The thermodynamics of the hyperuniform state are studied and found to greatly enhance the melting point of the low density amorphous phase.

The dynamics of the amorphous and liquid phases of Germanium are studied in Chapter 4. This is the first DFT based study of the dynamics of Germanium and it is demonstrated that the low density liquid phase is metastable on a time scale sufficient to demonstrate it has the dynamics of a liquid. Time and density dependent correlation functions are used to characterize the atomic scale motions of both the high and low density liquid phases.

Chapter 2: Cerium - Two Liquid Phases

2.1 Background: Cerium Electronic State and Structure

Bulk Cerium (Ce) is known to exist in two electronic configurations, trivalent Ce^{3+} and tetravalent Ce^{4+} . The transition between these two states is observable in the crystalline $\gamma \rightarrow \alpha$ phase transition that occurs near 1GPa at room temperature. This phase transition is isostructural, meaning that both phases have the same symmetry and the same composition. Both the γ and α phases are Face Centered Cubic (FCC), the only differences between them is a volume difference of 17%. The thermal expansion coefficient of the two FCC phases differs such that upon heating the volume difference gradually disappears. At 2GPa and 600K the two phases are identical, an occurrence referred to as a critical point. Ce is the only known element with a solid-solid transition ending in a critical point [31].

Liquid polymorphism is typically associated with a change in density between the two liquid phases. Because the α and γ phases of Ce exhibit a large density difference due to an electronic transition, it is possible that these changes persist into the liquid form. From figure 2.1 we see that the slope of the melting temperature as a function of pressure of Ce switches from negative to positive at 3.3GPa. The thermodynamic consequences of this change, as discussed in Chapter 1, are that the liquid must have a higher density than the solid phase an indication of liquid polymorphism. Ce is a logical material to search for a LLPT because of its negative melting curve and its unique electronic transition that causes a large volume difference between the α and γ phases. In this chapter a LLPT is investigated experimentally for Ce, the two liquid phases are explored through a study of the structure factor of the material. Finally the system is modelled using two unique model potentials and the PEL is probed through a free energy calculation.



Figure 2.1: Phase diagram for Cerium [2] with experimental data from this study overlaid in green triangles. Dotted lines are extrapolated from solid lines. The unlabelled phase at 0GPa and 200K is β . Of special interest here is the isotructural transition between γ and α phases and the negative melting curve below 3.3GPa.

2.2 X-Ray Diffraction Study of Liquid Ce

A critical method for experimentally investigating the structure of materials is to capture the Structure Factor directly through X-Ray Diffraction. The structure factor can also be solved for directly from simulation using the methods in Appendix A.1. This means the Structure Factor is a useful bridge for comparing simulation to experiment.

2.2.1 Experimental Method

The diffraction patterns presented here were generated at the Advanced Photon Source synchrotron at Argonne National labs. A diamond anvil cell was used to house the material and control pressure, lasers were used to heat the material. A diagrammatic explanation of the experimental setup is shown in figure 2.2a. The incoming beam (A) passes through a half silvered mirror (B) through the diamonds and and is incident on the material of interest (C). The experiment is setup such that the beam only diffracts with the material of interest and simply passes through the diamonds and half silvered mirror. The now diffracted beam exits the DAC and is gathered on a detector (D). A laser (shown in red) reflects off of the mirrors and is incident on the material, this is how the material is heated above its melting point. The pressure is controlled by mechanically squeezing the diamonds together inside the DAC.



Figure 2.2: a) Experimental setup for X-Ray diffraction. Discussed in text. b) Typical diffraction patterns. In the top image a bright halo shows that a liquid is present, the bottom image shows only crystals.

Diffraction patterns are generated following Bragg's law [32];

$$2dsin\left(\theta\right) = n\lambda\tag{2.1}$$

where d is the spacing between atomic planes, θ is the angle between incident beam and the crystal plane, λ is the wavelength of the beam and n is an integer describing the penetration depth of the beam. Armed with this equation and the basic knowledge of the experimental setup we can explain the resulting diffraction patterns observed in 2.2b.

The diffraction experiments are performed on powdered materials, so there are many randomly oriented crystals present in the beam's path. This random orientation causes narrow rings to form in the resulting diffraction pattern. Crystals have a fixed lattice spacing and diffract a narrow beam which then appears in the pattern as a narrow ring. This is in contrast to a liquid which generates a much broader and diffuse ring. This is because liquids have a broad range of bond lengths. Thus, in the top of figure 2.2b we can plainly see that there are several narrow peaks (due to the pressure calibration crystal which does not melt), and a single broad halo that is caused by a liquid. By integrating the diffraction pattern about the azimuthal angle we can obtain the corresponding Structure Factor.

The diamond anvil setup combined with laser heating is a powerful method that allows us to control the pressure and temperature of the sample. In particular the laser heating is convenient because it can access temperatures in the range of 1000K-2000K around the melting point of Ce. There is however a large source of error involved in calibrating the temperature and pressure sensors resulting in errors on the order of $\pm 100K$ and $\pm 0.5GPa$.

These experiments involved two beam line sessions, diffraction patterns were recorded at 1.9GPa, 13GPa and 22GPa. Cerium is an exceedingly difficult material to study with laser heating because it so easily oxidises. While carrying out the experiments we found that the high temperatures induced oxidation almost instantaneously so it was necessary to load the sample in an Argon environment in an attempt to limit the presence of O_2 in the anvil cell. However the seal between anvil cell and the atmosphere slowly degrades as heating takes place, effectively placing a time limit on the length of the experiment. Once laser heating was initialized we had approximately 1 hour to perform the experiment before oxidation ruined the material. The temperature ranges studied were chosen to maximize the breadth of sampling of the phase diagram in the hopes of seeing a volume change in the liquid before oxidation could take place.

2.2.2 Analysis Methods

Having gathered diffraction patterns at several pressures it is necessary to process the data into something that is easy to analyse. Software provided by Argonne National Labs, called FIT2D [33–35], is used to analyse the raw patterns generated by the experiment. Using FIT2D we can integrate the diffraction patterns and generate a raw structure factor such as the one showen in figure 2.3.



Figure 2.3: An unprocessed structure factor, the halo of the liquid is reduced to a broad gaussian at $q = 8\text{\AA}^{-1}$. The challenge here is to extract the liquid peak so it is possible to analyze it further.

From the structure factor it is possible to deduce which crystal structure is responsible for generating which peak. This is a long and tedious process that is done manually when the pattern is convolved with a liquid structure that makes automatic peak detection too difficult.

The problem of extracting and identifying the liquid structure factor is addressed here. The goal is to extract the liquid peak by assuming the total structure factor is a sum of the elements;

$$S_{total} = S_{background} + S_{crystals} + S_{liquid} \tag{2.2}$$

The crystalline and liquid peaks take a Gaussian form because their width is due to temperature fluctuations which take a normal distribution. We are not interested in the background, only in eliminating it so we can assume it takes some arbitrary form and remove it. The process of fitting these curves is straight forward and achieved using the tool fityk [36]. As shown in figure 2.4 fityk allows us to overlay an arbitrary set of curves on top of the data, then sums up those contributions and generate the total error between the data provided and fitted curves. A simple linear optimization routine is used to ensure the provided curves minimize this total error.



Figure 2.4: A screenshot from fityk, the tool used for fitting curves to the experimental structure factor. The raw data is highlighted in green, individual gaussians and other curves added by the user are shown in red, the sum of the user added curves is shown in yellow. The error between the experimental data and fitted curves is shown below.

Using this method the curve representing the pure melt can be isolated. Knowing the location and width of the melt Gaussian tells us the density of the liquid and the variance on its bond length. This is critical for identifying unique liquid phases and uniquely characterizing them.

2.2.3 Results

The liquid structure of Ce was probed at 1.9GPa, 4GPa, 13GPa and 22GPa. The analysis focuses on the 3 primary results at 1.9GPa, 13GPa and 22GPa which were the cleanest and most straightforward results. The experiment process can be followed by reading from a-e in figures 2.5, 2.6, and 2.7.

1.9GPa - Results

Two heating cycles were performed at 1.9 GPa, (a-c) and (d-f). Quenching (d and f) results in pure α phase reforming, excluding the possibility of oxide melt.


Figure 2.5: Experimental results at 1.9GPa. Two heat/quench cycles are presented.

Temperatures marked by * were estimated using the oxide peak positions combined with the thermal expansion measured at high pressures and temperatures. Example diffraction patterns are given for the melt(g) and final quench (h).

13GPa - Results

A single heating and quenching run was performed at 13GPa. Oxide was present before melting took place and the same amount of oxide is present upon quenching. Note that the oxide does not melt, this is commensurate with the literature melting point for CeO and CeO_2 which both melt above 2500K [37]. Upon quenching the cerium returns to its initial crystalline phase with a slight change in volume.



Figure 2.6: Experimental results at 13GPa.

22GPa - Results

This time melting takes place from the ϵ phase. Some oxide grows as the sample is heated, the location of the beam was adjusted to account for this (e). Upon quenching the material returns back to the ϵ phase.



Figure 2.7: Experimental Results at 22GPa.

2.2.4 Experiment Discussion

At 1.9 GPa the melt, characterized by a broad Gaussian shape curve, is centered at 2.19\AA^{-1} and no obvious shift of this main diffraction peak was found (except for a small peak shift resulting from thermal expansion), suggesting that the structure of the liquid phase is rather stable at this pressure. At 13GPa the main diffraction peak begins at 2.46\AA^{-1} and quickly shifts with increasing temperature to 2.34\AA^{-1} . From these peak shifts the volume collapse is estimated to be 14% and is associated with a change in density of the liquid phase, this is shown in figure 2.8. The 1550K curve (yellow) is a high density liquid (HDL), centered at a higher Q and is denser than the curve at 1900K (purple). As heat is applied the structure quickly moves towards a lower Q associated with low density liquid (LDL). At 22GPa the melt forms at 2.52Å⁻¹ and gradually moves to 2.46Å⁻¹. From these results it is believed that LDL is present at 1.9GPa and above approximately 1750K at 13GPa. At lower temperatures at 13GPa and 22GPa a HDL phase is present. As temperature is increased at 22GPa the HDL phase slowly expands approaching the LDL phase but not transitioning to it. The significant change in rate of expansion implies the existence of a critical point at which the LDL and HDL phases merge.



Figure 2.8: Structure Factor of the liquid at 13GPa. The liquid portion of the curve has been colored, the crystalline peaks remain as dotted black lines.

2.3 Simulations

Further study of the liquid-liquid phase transition is made possible through the use of computational models. It is necessary to choose a suitable approximation for describing the electronic states of Ce. Density Functional Theory (DFT) based simulations are a reliable and necessary method for simulating the two individual valence states of Ce, however it is not possible to accurately describe the transition or coexistence of these states using DFT. Separately the trivalent and tetravalent states can be accurately modelled, energies and densities are accurately described. Thus the model used here employs two separate systems to describe Ce and we refer to them as Ce^{f_0} and Ce^{f_1} . The Ce^{f_0} state is trivalent, the 4f electron is treated as part of the core and does not participate in bonding. The Ce^{f_1} state is tetravalent and the 4f electron belongs to the valence set. Under this approximation Ce^{f_1} will never transition to Ce^{f_0} , as will the reverse. The Ce^{f_0} and Ce^{f_1} accurately describe the real Ce^{3+} and Ce^{4+} states respectively, they are limited only by their inability to accurately describe the transition between the two states.

While DFT is accurate and valuable as an ab - initio method, it is computationally demanding and limited in the size of the system it can describe. These DFT simulations of Ce^{f_0} and Ce^{f_1} were found to be limited to a size of 100 atoms on the computational resources available, the time scale of these simulations was limited to 100's of picoseconds. In order to expand the size of the simulation and enhance the time scale a pair of model potentials have been developed. By eliminating the need to solve Schrödinger's equation for a system with hundreds or thousands of electrons the simulation is greatly simplified. Using this method the free energy of the two liquid phases is calculated, a coexistence line is found, and a critical point is predicted.

2.3.1 Ab-Initio Methods

As already mentioned our computational methods are limited and require modelling Cerium as two individual states, here we discuss these limitations and the results of these methods. In the Ce^{f_0} state a single f-electron is forced into a lower energy level, joins the core electrons that do not significantly contribute to bonding with neighboring atoms. This electronic state manifests in the crystalline γ phase of Cerium [38]. In the Ce^{f_1} state the lone f-electron join the $[5d_1 + 6s_2]$ valence electrons and actively contributes to bonds. The α phase of Cerium exhibits this electronic configuration [38].

To represent these two states accurately within the DFT framework two pseudo-potentials are needed. These pseudo-potentials describe the exchange-correlation contribution to the total energy. The Generalised Gradient Approximation (GGA) was selected for its accuracy in predicting the lattice properties of both the α and γ crystal phases [4].

Just because a method is capable of reproducing the crystalline properties of a material does not mean it is appropriate for modelling that material's liquid behavior. That said, there is little empirical data on the dynamics of liquid Cerium, certainly there is no data available concerning the multiple liquid states found here. So we are currently restricted to verifying the data generated by our own experimental studies, in particular confirming the structure factor of the material or its inverse Fourier transform, the Radial Distribution Function (RDF) at the corresponding temperatures and pressures. Methods for calculating the RDF and SF from simulation are given in Appendix A.

2.3.2 Ab-Initio Results

Liquid Cerium is produced in NVT simulations of 108 atoms which was initialized on a 3x3x3 super-cell of FCC α or γ Cerium depending on whether tetravalent or trivalent Cerium is being modelled. The simulation is heated to 2000K and annealed for 5ps, a temperature and time scale appropriate forming a liquid. The melt is verified by inspection ensuring disorder is achieved. The liquid is then cooled to the desired temperature and annealed for another 25ps. The pressure of the final liquid is manipulated by altering the volume of the initial unit cell and following the same process described above.

In figure 2.9 two completely distinct liquid structures are shown. At low pressures the Ce^{f_1} liquid maintains both short (2.9Å) and long (3.5Å) bonds, as pressure is applied these



Figure 2.9: Charge density isosurfaces from ab-initio simulations (top) and radial distribution functions (bottom) for Ce^{f_1} (a) and Ce^{f_0} (b) at a range of pressures. The short bonds present in Ce^{f_1} liquids are shown as solid rods, corresponding to the shoulder centered at 2.9Åat 0.6GPa in the radial distribution function.

two peaks combine, eliminating the long bonds entirely. Short bonds are associated with 90 deg angular bonds, as is shown in the isosurface plot in figure 2.9a, these bonds are shown as red rods. Trivalent liquid Ce^{f_0} is characterized by a long bonds in the first shell, centered at 3.6Å. As pressure increases the entire structure shrinks with little change in the 2nd and 3rd shells. Further distinctions between the two phases are found in the 2nd shell, Ce^{f_1} has a split 2nd shell at all pressures while Ce^{f_0} has a coherent 2nd shell whose shape is sensitive to pressure.

At all pressures Ce^{f_1} is the HDL owing to its electronic structure, while Ce^{f_0} is the LDL. These two distinct liquids are found at all pressures investigated. This is strong evidence for confirming the experimental data presented above, although further study is necessary to calculate which phase is energetically stable. While finding two distinct liquid phases is not entirely surprising given that these materials have different valence states, it is surprising how easy it is to form the distinct structures. Within their respective valencies these are clearly the dominantly stable liquid phases, they are easily formed from fast quenches and anneals (on the order of 10's of picoseconds) and their general topology can be captured in small simulation cells (with only 108 atoms).

2.3.3 Model Potential Methods

Using the model developed above we would like to determine the transition line between the two phases and see if a liquid-liquid critical point is predicted. This can be determined from the free energy of the LDL and HDL. A model interatomic potential for Ce^{f_0} and Ce^{f_1} will enable longer and larger simulations that are required for thermodynamic integration and for the development of an analytical function for evaluating the free energy.

Cerium is a metal under the conditions of interest and requires a potential that can describe the energetics of the electron sea as well as the pair-wise interactions that are present in metals. The Embedded Atom Method (EAM) [39] is a potential that was developed for this purpose. It is spherically symmetric and composed of a background electron density contribution and a neighbor pair interaction term. The total cohesive energy of the EAM potential is;

$$V_{tot}^{EAM} = \sum_{i} F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{i} \sum_{i \neq j} \phi(r_{ij})$$

$$\bar{\rho}_i = \sum_{j \neq i} \rho_j(r_{ij})$$
(2.3)

where ρ is a function describing the local electron density, F is the embedding function, and ϕ is the pair interaction term. In this function we introduce the standard notation for potential energy functions as a function of the distance between two atoms, r_{ij} .

To create a potential we must generate the embedding function F, the pairwise interaction function phi and electron density function $\bar{\rho}$. The fitting process described in Appendix B.2 was followed to create these functions.

Model Potential Results

Because we are unable to model a mixture of tetravalent and trivalent Cerium in the DFT simulations it is not possible to build a complete force database to describe a single model potential that describes all Cerium configurations. For this reason two potentials were built that model the trivalent and tetravalent states at all relevant thermodynamic conditions. Again, no mixing can take place between these two potentials. Refer to Appendix B for a detailed description of the potential models and how they are generated.

To verify the EAM potential's ability to accurately model these two phases we compare structural information recorded from the X-Ray diffraction experiments described above with RDFs and SFs generated with the relevant potentials. Molecular Dynamics simulations of 32,000 atoms were carried out under NPT conditions at a range of temperatures and pressures to produce liquid structures corresponding to those recorded experimentally. They are generated in a manner similar to the one described in section In figure 2.10 the agreement between the experiment and simulation can be demonstrated from the peak position and shape of the structure factor. The agreement between the experimental and simulated structure factors is satisfactory, showing the existence of LDL liquid at low pressures.



Figure 2.10: The liquid structure of Ce at low pressures corresponds to the trivalent state, the simulated structure factors of which are plotted against scattering vector Q at designated pressures and temperatures. The experimental data were obtained by Waseda [3]. In the bottom panel, the experimental structure factor at 1.9 GPa was optimized from the extracted peak data, the difference in shape from figure 2.8 is that the structure factor is corrected to remove the compton scattering contribution. The algorithm for structure factor optimization can be found in [4].



Figure 2.11: The structural evolution of HDL and LDL EAM Cerium as a function of pressure. These results closely match the DFT results in figure 2.9. The shoulder present in HDL is absorbed into the primary peak of the first shell as pressure exceeds 3GPa. The primary differences between the EAM and DFT results lay in the 2nd shell where the split 2nd peak of LDL is not manifested. This is interpreted this to mean the EAM liquid is more structurally uniform in the medium range.

Analysis of Combined Experiment and Simulation Results

With the introduction of the EAM potentials we can now fully interpret the experimental results produced above. The results are presented in figure 2.12 and they include 1.9GPa, 13GPa and 22GPa pressures over the temperature ranges provided. Corresponding simulation results are generated at the appropriate temperature.

Now we can clearly see that at 1.9GPa the (relatively) low temperature liquid matches closely with the central peak of the Ce^{f_0} LDL, it seems to be stable as a function of temperature.

At 13GPa the structure is closely aligned with the Ce^{f_1} HDL at low temperatures but as it is heated to 1900K the first peaks transitions to a lower Q value (corresponding to a lower density) and begins to line up with the Ce^{f_0} LDL. The transition seems to be rather sudden as the lowest temperature (yellow-1500K) quickly levels out by the 3rd curve (red-1600K).

Finally at 22GPa the first peak also lines up with the HDL generated in EAM, and as it is heated up it seems to slowly move towards a lower Q value, corresponding more closely to the LDL phase. However this transition doesn't finish and appears to continue even at above 1900K, this might imply that this is a 2nd order phase transition in the super-critical regime.

Having demonstrated strong structural agreement between EAM based simulations and semi-empirical we now calculate the free energy of these phases.

2.3.4 Free Energy Calculation

Molecular dynamics simulations were performed to calculate the free energy of the individual phases and the energy associated with their mixing. Free energy is a valuable parameter to know because it tells us which phase is more energetically stable and therefore which (or how much of each) phase will be present under certain conditions. With an analytical function for the free energy dependent on temperature, pressure and the quantity of each phase, we can then predict the stability line between the two phases and the location of a critical point.



Figure 2.12: The structure factor from the X-Ray diffraction experiments is presented (a,c,e) in comparison with the structure factor of the HDL and LDL liquids (b,d,f). Within this framework each experimental result is interpreted as being either HDL or LDL. In the case of 13GPa we can actually see a transition from HDL to LDL as temperature is increased.

The model developed thus far contains two independent phases, in order to calculate the free energy we must be able to combine them. To this end a transition model is employed. However the nature of the electronic transition that takes place during the crystalline $\gamma \leftrightarrow \alpha$ iso-structural transition is not entirely understood. The physics of the transition is still under debate in the literature, with two prevailing models providing possible explanations.

The Mott transition model involves an electron-electron screening that allows the valence f-electron to drop to a lower energy core state. This transition is stochastic such that both itinerant and localized atoms would be present in the material at one time [40].

The second model assumes the Kondo effect is responsible for the volume collapse [41]. This transition involves interactions of magnetic impurities which strongly contribute to the cohesive energy of hybridization states [41].

It is not within the scope of this study to determine which model is correct or appropriate, in fact either model could be used to describe the nature of the LDL \leftrightarrow HDL transition found here. The Mott transition model was chosen because it results in the most direct calculation of the free energy.

Within the Mott framework we can treat Cerium as a pseudo-alloy, meaning it is a mixture $Ce_{1-x}^{f_0}Ce_x^{f_1}$ where x is the relative quantity of Ce^{f_1} . The Gibbs free energy of our system is taken to be the sum of the free energy of the individual components and some associated mixing energy;

$$g(P,T,x) = xg_{f_1}(P,T) + (1-x)g_{f_0}(P,T) + g_{mix}(P,T)$$
(2.4)

This model was further refined by Aptekar and Ponyatovsky [42] and is defined by a regular solution model;

$$g(P,T,x) = xg_{f_1}(P,T) + (1-x)g_{f_0}(P,T) + u_{mix}x(1-x) + k_BT \left[xln(x) + (1-x)ln(1-x)\right]$$
(2.5)

which replaces the naive mixing term with a heat of mixing, u_{mix} , and interface energy



Figure 2.13: Free energy curves for the Cerium EAM 2 phase mixture described in equation 2.3.4. In subplots (a,b,c) the free energy is evaluated at the corresponding experimental pressures of 1.9GPa, 13GPa and 22GPa. These free energies curves are evaluated at temperatures 1200K, 1500K and 1800K corresponding to the blue, yellow and red curves. In subplot (d) the free energy is evaluated as a function of composition. Pressures and temperatures are chosen along the coexistence line. The composition at which the free energy is minimized are highlighted by white circles and connected by a green line to find the critical point at which the 2 minima per pressure-temperature are reduced to a single minimum. This happens after the 21GPa curve and is highlighted by a star.

contribution. The free energy functions g_{f_1} and g_{f_0} for the independent phases is calculated using the thermodynamic integration method which is described in Appendix C. The heat of mixing constant is set at $u_{mix} = 370 meV$, and is generated from fitting the curve $u_{mix}x(1-x)$ to the calculated mixing energies taken from DFT and EAM simulations. These mixing energies are found to be independent of temperature and slightly dependent on pressure but well within the range of acceptance up to 10GPa. We now have an analytical function for describing the free energy of the two phase LDL-HDL mixture.

In figure 2.13 several free energy curves are evaluated. First in sub-figures a,b and c the composition which minimizes the free energy at the experimental temperatures and pressures of interest is evaluated. At low pressures the LDL phase dominates, as pressure is increased to 13GPa a transition can take place as temperatures increase past 1800K (red curves). At 22GPa the optimal composition is slowly decreasing from purely HDL as temperature increases.

Figure 2.13d demonstrates that the transition between LDL and HDL is first order below 21.3GPa. This must be the case because at lower pressures there are two optimal compositions, one that is predominantly HDL and another that is LDL. At a fixed pressure the temperature will determine which of the two phases exists. Above 21.3GPa the two separate phase minima connect and only one dominant compositional minima exists. This point, (21.3GPa and 2100K) is referred to as the critical point because it is the point above which a distinction between the two liquid phases is no longer possible. Above the critical point the transition between the two phases is continuous or 2nd order in nature.



Figure 2.14: The phase diagram for Cerium is overlayed with the compositionally stable liquid phase as determined by the free energy function 2.3.4. The experimental data is overlaid in green. The LDL \leftrightarrow HDL transition line is highlighted in grey (becomes dotted in the metastable zone) and terminates at the liquid-liquid critical point.

These results can also be interpreted from the perspective of the phase diagram, as in figure 2.14. The composition which minimizes the free energy at the corresponding pressure and temperature is highlighted, red corresponding to LDL and blue for HDL. The critical point for the two liquid phases mimics that of the critical point for the two crystalline phases in that it terminates from a positive slope in dP/dT. The 1.9GPa results are squarely in the LDL zone, the 13GPa results cross the transition line and the 22GPa results slowly traverse the supercritical transition zone.

2.4 Summary

In this chapter we have reviewed an in depth study of the first experimentally observed monatomic liquid-liquid phase transition [23]. The transition was found through a series of X-Ray diffraction experiments and later confirmed through extensive simulations. This includes a study of the materials using small scale DFT simulations which were then used to develop model potentials. These potentials enabled the efficient evaluation of the energy landscape so that thermodynamic integration could be performed and the free energy of the individual phases could be calculated.

A strong structural agreement between the liquids produced in simulation and experiment was found using the structure factor. The transition between LDL and HDL was justified using the free energy calculations and verified the transition pressures and temperatures found. This allowed a complete picture of the phase diagram to be obtained.

A critical point is predicted to exist beyond which the transition becomes 2nd order. This is an example of a stable liquid-liquid phase transition, an exceedingly rare occurrence only thought to happen in Selenium [43]. and Phosphorus [44,45]. Below the melting point the liquid-liquid transition closely follows the crystalline transition between the $\gamma \leftrightarrow \alpha$ phases.

Because the LDL and HDL are stable phases they are readily apparent over both short and long time scales, they do not suffer from competition with a lower energy phase. This also means they can be directly observed in simulations which was taken advantage here to verify the experimental results. This is an excellent example of the benefits of combining simulation with empirical data allowing each method to play to its advantages.

In later chapters the metastable liquid phases of Germanium will be investigated. This study will be contrasted with the stable liquid transition presented here, challenges will be compared and the importance of the results will be discussed.

Chapter 3: Germanium - Amorphous Structure

3.1 Stable and Metastable Polymorphism

Under ambient conditions Germanium is stable as a Diamond structure. In fact its low pressure stable phase diagram is simple, as seen in figure 3.1. The diamond structure transitions to a $\beta - Sn$ phase above 12GPa, melts at 1211K and vaporizes beyond 3106K. At high pressures there is debate as to what phases exist [5, 46, 47], although there is evidence that there are more than 5 stable phases present between 75GPa and 150GPa at ambient temperature. Furthermore if metastable states are considered Germanium takes on upwards of a dozen different phases [6], the number of metastable crystalline states is constantly growing [48].



Figure 3.1: The stable phase diagram of Germanium taken from reference [5]. The still contentious oS16, BC8, and ST12 structures are not shown.

A couple of the bulk metastable phases of Germanium can be formed when de-pressurizing the high pressure stable phase βSn . The rate at which pressure is removed from βSn offers different dynamics on its transition pathway to the stable cF8 phase and results in different metastable phases forming. This bizarre occurrence is due to Germanium switching between covalent and metallic bonding nature. There is also an unusually high energy barrier between dominant crystal symmetries making it possible for metastable states to be accessed [6]. This kinetically modulated transition can be pictured as hopping between a variety of local minima between the dominant stable Diamond and βSn minima. This kind of behavior requires a large energy barrier between dominant phases. While it may be the case that many other monatomic materials are capable of transitions like this, most of them lack a sufficiently large energy barrier to enable they quickly collapse to their most stable phase. Clearly the PEL of Germanium is very complex.

The presence of many high-pressure stable phases and low-pressure metastable phases is akin to the complex phase diagram of H_2O . Indeed Germanium and other semiconductors such as Carbon and Silicon share many structural and phase similarities with H_2O . This is due to water's tendency to form both a low density tetrahedral network and high density octahedral arrangement depending on its environment. These similarities go so far that a model of H_2O as a single component pseudo-atom that exists chemically between Carbon and Silicon has been developed and gaining some traction [49]. Water and Silicon are both known to have interesting amorphous and liquid properties as well, it is worth investigating Germanium to see how far these similarities extend.

3.2 Polyamorphism

Of particular interest is the negative melting slope in dP/dT of the diamond Ge phase. As discussed in the introduction, the Clausius Clapeyron equation 1.1.1 indicates that the negative melting slope is due to the notorious volume collapse upon melting. We are interested to see if this also indicates multiple glass phases and furthermore if the existence of multiple glassy phases coincides with the existence of multiple liquid phases. This reasoning stems



Figure 3.2: Some of the low pressure metastable crystal phases and their transition criteria, taken from [6]

from figure 1.3 in which the PEL indicates unique glassy phases can exist within mega-basins that are separated by an energy barrier. We are also interested in what the properties of these glasses and liquids are, do they have unique structural characteristics, and how they are most easily formed.

The stable liquid state of Germanium has been probed extensively through experimental methods [50–54], it seems evident that within the relevant pressure range (0-15GPa) above the melting temperature Germanium exists as one stable liquid phase. Because this liquid is more dense than the crystalline diamond phase and amorphous diamond phases we refer to it here as the HDL. If a second liquid phase does exist it would inhabit the metastable zone below the stable melting temperature and above the glass transition temperature. Metastable phases are notoriously difficult to study through experiment because they are prone to stabilization through melting or crystallizing and can exist on extremely short time

scales.

If a metastable phase exists within the confines of a high energy barrier it is possible that its relaxation time, e.g. the time it takes for the metastable phase to reach equilibrium, will be long enough that it can be experimentally observable. An example of a long lived metastable state is everyday Silica based window glass which is locked in a metastable disordered phase. Short lived metastable phases such as metallic glasses often collapse back into a crystalline phase on the order of nanoseconds. This short lifetime prohibits their study through current experimental methods which typically require a lifetime of several minutes in order to, for example, capture a coherent diffraction pattern of the material.

There are few experimental studies into the metastable nature of Germanium [7, 55], these are largely complicated by the tendency for the material to crystallize upon quenching or de-pressurizing. So we turn to simulation to probe the thermodynamics of the metastable zone.

3.3 Static Topology of Amorphous Structures

Before discussing the simulation method used to model the Ge system, we introduce here the methods employed to study disordered structures. The distribution function calculations and structure factor calculation are discussed in AppendixA.1, these tools are useful for investigating the bulk average structure of a material. There are caveats in which the ensemble structural behavior effectively hides critical behavior such as the formation of voids, crystal seeds, density fluctuations, and certain subtle disordered phase transitions. We need more refined tools to better study the disordered phases.

A method to characterize the distinct liquid and amorphous structures is also needed. In crystalline structures some form of symmetry is always present in addition to the size and shape of the unit cell and chemical ordering. In dynamic and disordered systems this symmetry is broken and only short range or in rare occasions medium range ordering is present. We are particularly interested in what differences in quenching rate, pressure, and annealing might have in these disordered structures. So the methods described below are critical in identifying and quantifying atomic reordering that are associated with bulk behavioral changes.

3.3.1 Coordination Number

The coordination number has an arbitrary definition. It is a count of the number of neighbors an atom has, more ideally it is a count of the number of bonds an atom has. In a molecule where all of the bonding characteristics are empirically known this is a straight forward calculation. Since we lack this information the per-atom coordination is defined as the number of neighbors about a central atom within the cutoff distance r_{min} . The cutoff distance is taken from the radius at which the first minima in the RDF is found.

$$n_{cn} = 4\pi\rho \int_0^{r_{min}} rg(r)dr \tag{3.1}$$



Figure 3.3: The radial distribution function with its first minimum highlighted. The integral from 0 to r_{min} is the average total coordination of a disordered system.

The process of finding the first minimum in RDF has been automated using windowed averaging and Newton's method on the first derivative of the RDF. The average r_{min} is used to calculate the per atom coordination. This is a flawed calculation because far away from equilibrium the variance of atomic bond lengths will be high and the coordination will be underestimated. However it is better than the alternatives such as Veronoi Tesselation [56] which greatly over estimates the number of neighbors. This is because Voronoi Tessellations of disordered systems result in a vast over estimation of the number of neighbors, including atoms that are several angstroms away.

It is also possible to calculate the coordination from the electron density, or Electron Localization Function (ELF) [57]. The ELF is a 3D scalar field where at each point the probability of finding two electrons of like spin at that point. Bonds can then be determined from basin interconnection points in the scalar field. However this requires costly calculations on a high resolution scalar field, and it was found that it is inappropriate to use on longer simulations with hundreds of thousands of time steps. Furthermore semiempirical potentials do not include information about electron density and so the ELF is not available for these types of simulations.

Due to its reliance on ensemble properties (r_{min}) the coordination number is insufficient to identify unique structural characteristics in the bulk of a liquid or amorphous phase. So we can see there are a number of computational challenges involving calculating the coordination number, and while it is possible to employ this naive approach it is desirable to have a more well defined order parameter for investigating our disordered structures.

3.3.2 Tetrahedrality

The stable Ge Diamond structure is composed of perfect tetrahedral units with 4 bond angles at exactly 109.5°. As will be elaborated later in this chapter, it is understood that the Ge amorphous structures are highly sensitive to the number of short range tetrahedral structures. So it is natural to seek out a function that is highly sensitive to this ordering. The Tetrahedral Order Parameter (TOP) has two components, angular and distance [58]. The distance portion for a single atom_i is defined as

$$S_i^{dist} = \frac{1}{3} \sum_{j=1}^{4} \frac{(r_j - \bar{r})^2}{4\bar{r}^2}$$
(3.2)

where the sum over j is looping over atom_i 's 4 nearest neighbors, \overline{r} is the center of mass of the 4 neighboring atoms and its central atom. The whole term is normalized such that the maximum value is 1 and the minimum value is 0.

The angular portion of the tetrahedrality is defined as

$$S_i^{ang} = 1 - \frac{3}{8} \sum_{j=1}^{3} \sum_{k=j+1}^{4} \cos\left(\Psi_{jk} + \frac{1}{3}\right)^2$$
(3.3)

with the double sums over j and k are over each possible angle Ψ_{jk} where the central atom_i is at the center of each bond angle. The angular term is normalized such that $S^{ang} = 1$ for a set of bonds perfectly coordinated at 109.5° and on average $S^{ang} = 0.5$ for a set of random angles that are typically seen in high temperature metallic liquids. The distance portion of the TOP is found to be superfluous in this study as the ideal bond length for a tetrahedral Germanium unit is fixed, so the TOP is taken to be S^{ang} alone which is common practice.

This is an effective method for identifying amorphous structures with Diamond characteristics. The high pressure stable phase βSn is characterized by a $S^{ang} = 0.6$.

The TOP suffers from similar numerical errors to the coordination number. By definition it considers only the 4 nearest neighbors where as chemically a Germanium atom may interact with up to 6 neighbors. Furthermore isolated Germanium atoms have been found in the liquid with no chemical bonds, but the TOP would completely ignore this because it puts no limitations on the maximum bond length and ignores the underlying electronic chemistry. These shortcomings must be taken into account when using tetrahedrality to study disordered structures.

3.3.3 Bond Orientation Parameter

A common problem when studying the metastable dynamic structures is determining whether or not a crystal seed has formed. This is particularly challenging in larger simulation blocks where the enthalpy will not change significantly when only a small portion of the material transitions to crystal. In visualizations of large simulations it is not possible to identify crystal seeds without the use of an order parameter to selectively color and highlight crystallized atoms.

The coordination number is insufficient for this purpose because both the low density crystal and amorphous Germanium phase are 4-coordinated. Similarly, LDA Germanium has a $TOP = 0.92 \pm 0.03$ which is very close to the TOP=1.0 for the diamond crystal. So a secondary method is needed to confirm the existence of crystal seeds when one is suspected of forming during a molecular dynamics simulation.

The Bond Orientation Parameter [59] (Q_l) is defined;

$$Q_{l} = \left(\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{Q}_{lm}|\right)^{\frac{1}{2}}$$
(3.4)

where,

$$\bar{Q}_{lm} = \frac{1}{N_b} \sum_{j=1}^{N_b} Y_{lm}(\theta(\vec{r}_j), \phi(\vec{r}_j))$$
(3.5)

 Y_{lm} are spherical harmonics of the angles θ and ϕ for the *j*th bond $\vec{r_j}$. N_b is the number of bonds. Again the term bond is not taken from the real chemical definition, instead two atoms are considered bonded when the distance between them is less than the cutoff distance. Here the cutoff is taken from the first minimum of the radial distribution function of the system, the same as r_{min} in the coordination number calculation.

Non-zero values for Q_l are found when l = 4 for cubic ordering and when l = 6 for icosahedral ordering. The special case l = 3 is associated with tetrahedral ordering, specifically



Figure 3.4: The same amorphous structure is shown with atoms colored by Q_l with the l-value given. A crystal seed is present in the upper lefthand side of the simulation and is most clearly highlighted by the l = 3 case.

those with bonds at 109.5°, however it is overly sensitive [58] and not commonly used. Certain values of Q_l correspond to orientation ordering, and a range of crystal symmetries (FCC, BCC, SC, Hex, Icosahedral, etc.) can usually be identified using just a combination of Q_4 and Q_6 . This makes the bond orientation parameter particularly useful for discerning disordered states from crystals and high temperature liquids.

From figure 3.4 we see a common situation from a long time anneal of a 1728 atom simulation using the Stillinger-Weber potential. A liquid system under NVT (constant number of atoms, volume and temperature) conditions is cooled below its freezing temperature and held in super-cooled state in an effort to explore its dynamics. However a crystal seed has formed, this is an ideal situation to study the effectiveness of Q_l at various l values. Only with l = 3 is the bond orientation parameter able to highlight the diamond crystal seed, even this is spurious and if the crystal seed is oriented in the wrong direction or is heavily defected (as is common at high temperatures) than it may not be detectable.

The bond orientation parameter is used in combination with the tetrahedral order parameter to confirm the presence of crystal seeds or variations in the local structure of disordered materials. It is likely the case that for other materials that crystallize to cubic or hexagonal symmetries the bond orientation parameter is sufficiently sensitive for demarcating the structural variations.

3.4 Simulation Method

Germanium's metastable amorphous phases require a high fidelity computational method that includes electronic interactions. The DFT as employed by VASP [9,60], using projector augmented wave (PAW) pseudopotentials [61] is a suitable although computationally demanding method for studying disordered Germanium.

While many semi-empirical potentials are available through the literature severe short comings were found which made these potentials inappropriate for this study. A thorough discussion of these potentials and why they are inappropriate for this study is available in Appendix B.3. The crux of this point is that semi-empirical potentials are useful in studying the underlying structure of already known phases, not predicting the existence or stability of new phases.

Liquid Germanium was first studied by Kresse and Hafner in the seminal work describing the operation of the VASP software package [60]. In this case the Germanium system was chosen because of its varying electronic state, the difficulty in accurately describing its liquid structure and its similarity to the extremely popular Silicon and H_2O systems.

The Generalized Gradient Approximation (GGA) with Perdew, Burke, Ernzerhof (PBE) functional is used in these simulations because of its accuracy in describing the many crystalline and metastable states of Germanium [62, 63]. While the GGA functional alone has also been used in liquid Germanium studies [60, 64] it was found here that these two methods produce virtually identical liquid and amorphous structures an example of their similarities is shown in figure 3.5. Good agreement between these two

3.5 Formation of Amorphous Structures

A simulation block size of 144 atoms was constructed, this small simulation block is used solely for the purpose of exploring the thermodynamics of the material. All of these molecular dynamics simulations are performed under canonical environmental controls, with fixed



Figure 3.5: One example of the many nearly identical results in a comparison of the PBE-GGA and GGA funcationals for high temperature (750K) LDA Germanium structures. PBE is green and GGA results are blue here. The black circles are taken from Etherington's experiments on vapor deposited Germanium [7].

number of atoms, volume and temperature. Canonical ab-initio molecular dynamics operate by calculating the forces at each time step, calculating the corresponding velocities through Newton's equations of motion and then scaling the velocities in order to maintain the desired temperature.

A series of quenches are carried out at several volumes and at various rates. The term quench refers to the fast decrease in temperature the material undergoes starting from a liquid state. The goal in quenching is to avoid the stable dynamics that govern slow processes. Through quenching the crystal transition is avoided and a solid amorphous phase is formed. Through this process we will observe and investigate the transition between the liquid and amorphous states. In these simulations a 5fs time-step is chosen, this is the largest time step possible without accruing significant numerical errors.

These liquid states are prepared by annealing for 2000 time-steps, or 10ps, above the melting temperature at several densities. The enthalpy curves of fast quenches at rates of



Figure 3.6: The enthalpy as a function of temperature during quenching, on the left at 120 K/ps and on the right 8 times faster at 15 K/ps. All extensive variables are given in per-atom units. The legend shows the volume per atom for each simulation.

120K/ps and 15K/ps are shown in figure 3.6.

The 120K/ps quenches are too fast and they end up forming the inherent structure of the liquid, the quench rate is so high it doesn't give the liquid any time to relax. At 15K/ps there are several salient features that indicate phase transitions and interesting effects occurring. There is a sudden drop in the enthalpy at 18 Å³ (blue curve) while at 20 Å³ the enthalpy seems to linearly decrease with temperature. At 22 Å³ and 24 Å³ the enthalpy slowly increases below 500K, while at 26 Å³ the the volume linearly decreases.

Crystallization

The sudden drop in enthalpy at high pressure (18 Å^3) is due to a crystal phase transition into the tI4 crystal structure, this happens to be the stable high pressure phase for Ge. To avoid this phase transition the quench must occur at unreasonably fast rates, this is an unstable pathway for forming the high pressure amorphous state. This is in strong agreement with vitrification experiments which show it is not possible to quench bulk Germanium fast enough while under pressure (above 5GPa) to form a glassy phase [55], while at low pressures the glass is readily formed from laser heating and subsequent quenching. No crystal seeds were found in any other samples presented here, this was confirmed by inspection of the final structure using TOP and Q_l .

Voids

At sufficiently low pressures the liquid will begin to transition into a vapor. Near this transition line the gas transition manifests as the formation of large gaps in the structure known as voids. The formation of voids allows the rest of the material to maintain a higher density as is visible in the 26\AA^3 quench where the enthalpy linearly decreases.



Figure 3.7: (a)The TOP against the temperature corresponding to the 15K/ps quenches in figure 3.6. The TOP of the voided 26 Å³/atom structure is higher than the 24 Å³/atom amorphous sturcture with no void. (b)The voided 26 Å³/atom structure with void highlighted in yellow, the coloring is according to the coordination number.

Void formation is a direct result of this being a fixed volume simulation trapped beyond the vapor stability line. At the atomic volume 24 $Å^3$ /atom the amorphous Germanium is composed of 4-coordinated local structures that are low in density and are evenly distributed through the simulation cell. At higher atomic volumes excess volume is introduced, and at high temperatures this excess volume is able to coalesce into a void. Quenching a voided liquid arrests the dynamics such that the void will still exist as the stable tetrahedral arrangement begins to form. This creates an uneven distribution of the density at low temperatures.

This is exactly the process observed in the 16K/ps quench at 26 Å³/*atom*, the final structure is shown in figure 3.7b. Interestingly the 26 Å³/*atom* structure has a higher tetrahedrality than the $24\text{Å}^3/atom$ structure, this is likely due to the stochastic nature of quenching and the formation of the low density amorphous phase.

As is shown in figure 3.9a the 26 $Å^3/atom$ structure is very similar to pure LDA but with an enhanced first peak and larger gap. Clearly the void doesn't destroy the short range ordering but enhances it. Voided structures showing a larger gap between the first and second shell is evidence that the LDA produced by Etherington [7] through vapor deposition is in fact voided.

This void model follows the van Der Waals equation of state [8];

$$\left(P + \frac{a}{V^2}\right)(V - b) = k_B T \tag{3.6}$$

which is an extension of the ideal gas law. It takes into account repulsive atomic interactions, a, and the effective volume of the atoms, b. Isotherms shown in figure 3.8 reveal the stable existence regions of the liquid and vapor as well as a coexistence zone which is found through the equal area equation;

$$P_V \left(V_G - V_L \right) = \int_{V_L}^{V_G} P dV \tag{3.7}$$

where P_V is the vapor pressure, G and L subtexts refer to the gas and liquid phases respectively.



Figure 3.8: The van Der Waals equation [8] is used to predict the coexistence (blue zone) and dominant liquid (green) and vapor (yellow) zones.

3.5.1 LDA and HDA

From the sequence of quenches at least two unique structures seem to be present, the collection of RDFs is shown in figure 3.9a. At high densities the inherent structure of the liquid has a tetrahedral order parameter near TOP = 0.6. We cannot yet label this structure as HDA because the quenching process used is too fast for the material to relax. Also quenching at these pressures is also prone to crystallization. Another method is needed to attain the HDA structure and to observe the LDA-HDA transition.

A void-free LDA structure is attained at 24 $Å^3/atom$ its RDF is characterized by a high first peak followed by a broad gap and a sharp second peak. This is indicative of the strong short range order present in LDA. The high first peak and subsequent gap implies that LDA is composed almost entirely of one first shell structure (tetrahedral units). This structure must be aperiodic because in the long range the RDF tends towards 1.0.

The high density structures have a first peak at a longer bond length, this coincides with an increased coordination number from 4 (LDA) to 6 (HDA).

The structure at 22 $\text{Å}^3/atom$ appears to be unique, its first peak is between the high density and low density structures, it also has a 3rd peak at a unique location. However we



Figure 3.9: (a)RDFs from the final structures of the quenches provided in figure 3.6. The 18 $Å^3/atom$ and 20 $Å^3/atom$ quenches were taken from the 120K/ps simulations. The other volumes were taken from the 15K/ps quenches. (b) The $22Å^3/atom$ structure overlaid with a mixed RDF, discussed in the text.

can show that by mixing the high and low density structures we can reproduce this RDF (see figure 3.9b). This particular mix is made from 60% of the $20\text{\AA}^3/atom$ structure and 40% of the $24\text{\AA}^3/atom$ structure.

3.6 The HDA-LDA Transition

From the quenching method above we have run into a few problems; in order to avoid crystallization at high pressures we can only sample the inherent structure of the high density liquid, we have a unique intermediate structure forming at 20 Å³/*atom* and the question of void formation at low densities. To elucidate the bounds of these structural anomalies the structure at 0K is investigated.

The 144 atom structure from 20 $Å^3/atom$ was run through a conjugate gradient optimization routine to resolve its lowest energy arrangement. This is equivalent to an instantaneous quench to 0K or probing this structure's local minimum. The structure was then artificially perturbed by expanding its volume by 2% and then running it through another conjugate gradient optimization run. This process was repeated 20 times until a maximum volume was achieved and void formation was detected. The structure was then compressed, following the same optimization scheme. A closed loop was formed when, below $16\text{Å}^3/atom$ pressure induced crystallization occurred. During the expansion run the HDA slowly transitions to LDA, once the transition is complete the LDA follows its equation of state until voids being to form beyond 25Å^3 . Through the compression run the LDA again follows its equation of state until it begins to transition to HDA beyond 21Å^3 . The transition process was found to be reversible using , as the starting HDA phase is reformed near 16Å^3 . Results are summarized in figure 3.10.

Above $25\text{\AA}^3/atom$ voids begin to form in the LDA, however because the dynamics are constrained to those allowed by the conjugate gradient routine the voids never coalesce and their formation can be entirely reversed upon pressurizing. Upon compression LDA is begins to transition HDA below $23\text{\AA}^3/atom$ however the exercise of finding the precise transition pressure to compare with literature is left for a later section.

From this exercise we are able to generate HDA directly from applying pressure to and subsequently relaxing LDA in a piecemeal process. The transition process takes place between $20\text{Å}^3/atom$ and $23.5\text{Å}^3/atom$, although both LDA's and HDA's energy minima exist within the transition zone. The HDA formed here has similar TOP and nearly identical RDF to the $18\text{Å}^3/atom$ quench shown in figure 3.9a.



Figure 3.10: The Pressure (top), Cohesive Energy (middle) and Enthalpy (bottom) plotted against the volume for the 0K HDA-LDA transition of a 144 atom system. Each point is colored by its tetrahedrality the defected LDA is orange-red and the HDA is green. The corresponding values for the crystalline diamond (red) and βSn (blue) structures are overlaid.

3.6.1 LDA Quench Rate Dependence

This is a fixed volume canonical simulation a wide pressure range is sampled and it is necessary to choose a volume that minimizes the risk of void formation at low pressures and crystallization onset at high pressures. So the HDL liquid is quenched at a fixed volume of $24AA^3/atom$ at various rates to better approximate the HDL-LDA transition temperature. This is better known as T_g the glass transition temperature, since LDA is a glassy phase. At this fixed volume the HDL is at a negative pressure and the LDA is at a positive pressure, the average pressure between these two phases is near 0GPa though. The results are summarized in figure 3.11. A mixture of simulations from 144 atoms and 288 atom simulations are used to provide a complete picture.

From these results it is demonstrated that slower quenching rates result in a much sharper transition at higher temperatures. This is because the ensemble has more time to sample the temperatures near the transition pressure and is able to slide into its new energy minimum over a longer time range. During a fast quench the ensemble is effectively dragged over by velocities which are artificially decreased. From the trend of sharper and sharper transitions at higher temperatures we can predict that the phase transition occurs near 650K.


Figure 3.11: The Coordination (top) and Pressure (bottom) plotted against the temperature for several quenches. Slowest quenches (0.5E12 and 2E12 K/s) are done on 288 atom systems, all others are 144 atom systems.

3.7 LDA Annealing

The structure of the LDA has some critical discrepancies from the vapor deposited LDA observed in experiments [7, 65]. This is not entirely unexpected, the glass structure is difficult to form and defected in simulation. The glass transition itself is a stochastic process and the range of energies sampled is broad over the quench process followed above, most glasses formed will be artificial and locked in local minimum states that are far from what is formed in reality. Experimentally the gap between the first and second peak in the RDF hits values less than < 0.02 between 2.8Åand 3.3Å, the height and width of this gap is related to the presence of structural defects in LDA [65] and voids.

To better describe the LDA phase a 288 atom simulation is constructed and quenched at $24\text{\AA}^3/atom$. This density is selected from figure 3.10 because it is near the LDA cohesive energy minima and avoids the possibility of phase separation in the transition zone. At this density we expect to be able to explore the thermodynamics and structure of a pure LDA phase with no voids or mixing with HDA.

The 288 atom liquid simulation is cooled from 1250K to 850K and is slowly quenched to 450K at a rate of 2K/ps (8 times slower than the quenches in figure 3.6). The pressure presented here takes into account the thermal pressure and is defined $P = P_x + k_b T \rho$, where P_x is the external pressure.

From there the material is annealed at 450K for 50ps, this final structure was then annealed at 500K, 550K and 600K for 50ps. No significant transitions were observed since the glass is stable over these time scales. However at 650K dynamics were activated, to ensure a fully relaxed structure was formed the anneal was run for 250ps. Here the LDA undergoes a critical structural transition to a Hyperuniform LDA (HULDA). This transition is associated with an increase in pressure to 1.3GPa and ensemble TOP increases from 0.825 to 0.90. The pressure during the quench is shown in figure 3.12 as the blue curve, the anneals are shown in black. The HULDA transition occurs at 650K indicated by the black arrow. We refer to this structural change as hyperuniform because it eliminates



Figure 3.12: The slow quenching (blue) and annealing (black) and melting (orange) runs, as described by the Pressure vs Temperature. Colored arrows indicate the direction of the simulations. Glass formation is associated with a significant pressure increase up to 0.7GPa prior to annealing. Melting is associated with a pressure collapse to -1.7GPa at this density.

most of the defects in the material and also smooths out density fluctuations. In this thesis the term HULDA falls within the umbrella definition of LDA and may be mixed in with this term when appropriate.

Prior to the structural shift the as quenched LDA was found to melt above 625K, this in contrast to HULDA which survives over long anneal times at 730K with no sign of melting to the high density liquid. It is nearly impossible to attain the precise melt temperature from the dynamics employed here because melting is a stochastic process. Bounds can be set on the melting temperature from the anneal runs, melting takes place somewhere in the 'eye' shown in figure 3.12 because the glass transition occurs from a supercooled liquid and the melting process occurs from a superheated glass.



Figure 3.13: The structural evolution of the 600K during the LDA to HULDA transition. Atoms with TOP > 0.88 are not shown.

To better capture the micro-structural evolution of the glass as it transitions into the HULDA state a number of numerical tools are applied. In figure 3.13 the atoms are colored by their tetrahedrality. A temporal average is applied because at this temperature the tetrahedrality of each individual fluctuates about some average value. Averaging over 1000 time steps eliminates these fluctuations and captures the mean structural ordering.

The as quenched LDA structure at 600K (figure 3.13a) has an average tetrahedrality of 0.825 and is arranged as a central defect core with TOP at 0.72 and slowly increasingly tetrahedrally ordered shells. Annealing at this pressure enables thermally activated dynamics, over coming local energy barriers between neighboring states. Atoms are able to hop out of their confinement cages and tend towards more energetically stable states. This coincides with an increase in the tetrahedrality of the glass and its pressure. The pressure increase is expected as the tetrahedral units have longer bonds than the defects with a higher coordination.

3.8 Structure Factor in the Long Wavelength Limit

Historically the topology of glasses has been characterized as a Continuous Random Networks (CRN) [66]. This model dictates that atoms in a glass will adopt any arrangement that satisfy their local bonding needs and minimizes strain. This was associated with minimizing the variance in the shortest bond length and first shell bond angles. Recently more stringent parameters have been proposed for glass models, in particular for the amorphous Silicon and Silica models which are similar to Germanium [67]. The Nearly Hyperuniform Network (NHN) relies on the behaviour of the structure factor at long wavelengths.

In general the structure factor for a liquid is defined as

$$S(Q) = 1 + \int e^{-iqr} r G(r) dr$$
(3.8)

where $G(R) = 4\pi\rho r(g(r) - 1)$. So the long wavelength region of the structure factor, $S(Q \to 0)$, is related to the density fluctuations in a system by [68]

$$S(0) = 1 + \int rG(r)dr = \frac{\left[\left\langle N^2 \right\rangle - \left\langle N \right\rangle^2\right]}{\left\langle N \right\rangle}$$
(3.9)

this is a fundamental result of a grand canonical ensemble. The 288 atom simulation cell is only an approximation to the infinite volume grand canonical ensemble so S(0) cannot not be calculated directly and must be approximated. The RDF g(r) is defined only over the range $0 \le r \le L/2$ for a simulation cube with sides of length L.

It is remarkably difficult to generate model systems that conform to either the CRN and NHN standards [69, 70]. As shown in Appendix B.3 the semi-empirical potentials for Germanium largely lack the ability to reproduce a viable glassy structure through standard vitrification simulations.

It is possible to generate glass structures by doing away with molecular dynamics and turning to an algorithmic solution. Still, artificial models are difficult to generate because of the need to satisfy periodic boundary conditions. When slowly building up a randomly networked amorphous structure shell by shell the edge of the simulation box is eventually reached and at the boundaries one will always encounter imperfections [1]. There are some viable solutions and one model in particular stands out and has gained general acceptance as a straight forward algorithm for developing tetrahedral network glasses. In the section 3.8.2 this method is discussed and compared against the HULDA glass formed through the annealing method in section 3.7.

3.8.1 Calculating $S(Q \rightarrow 0)$

The details for calculating S(Q) in general are given in Appendix A.1. Because these simulations operate in a bounded volume these computational methods are not transportable for the long wavelength $Q \rightarrow 0$ region. In figure 3.14 the structure factor using the direct Fourier transform of the radial distribution function is given. The finite size oscillations are clearly visible at Q < 1.

We cannot extrapolate our S(Q) model from some small Q down to 0 because the error due to the finite size effect is deeply mixed with the underlying S(Q) and difficult to describe numerically. So we turn back to our definition 3.8 which is the integral over an infinite sampling volume, we can investigate the behavior of S(Q) over a new dimension, Rthe size of the sampling volume.

$$S(Q \to 0, R) = \frac{\left[\left\langle N(R)^2 \right\rangle - \left\langle N(R) \right\rangle^2 \right]}{\left\langle N(R) \right\rangle}$$
(3.10)

Torquato and Stillinger [71] used the work of Landau and Lifshitz to redefined the variance



Figure 3.14: The structure factor as computed from equation 3.8 the inset highlights the finite size effect which induces fluctuations at low-Q.

function N(R) in terms of the shape function $\alpha(r; R)$. The small r is the atomic coordinate distance and the big R is the volume of our variance sphere. The shape function is defined as

$$\alpha(r;R) = (1 - r/2R)^2 (1 + r/4R)$$
(3.11)

it is the volume intersection between two spheres of radius R that are separated by a distance r. So we are able to re-write equation 3.8 using 3.8.1 and arrive at the result [72];

$$S(Q \to 0, R) = \frac{\left[\langle N(R)^2 \rangle - \langle N(R) \rangle^2 \right]}{\langle N(R) \rangle} = 1 + \int_0^\infty r G(r) \alpha(r; R) dr.$$
(3.12)

The critical point here is that as $R \to \infty$ the function $S(Q \to 0, R)$ converges to $S(Q \to 0)$ as given in function 3.8. The shape function essentially acts as a dampener, perturbing the G(r) function so that at longer distances, $r \gg 1$, the convolution $G(r)\alpha(r; R)$ tends towards zero. We can now investigate the behavior of $S(Q \to 0, R)$ as $R \to 0$ safely from a computation stand point, and more accurately extrapolate to S(0). As with any numerical approximation there are some shortcomings, which we will see when this method is evaluated in later sections.

3.8.2 WWW Based Methods

The Wooten-Winer-Weaire (WWW) algorithm [73] was developed with goal of producing CRN that are tetrahedrally ordered in a computationally efficient manner. The method relies on the use of the Keating potential [74] which follows the form

$$V_{total} = \sum_{i < j} \left[\frac{3\alpha_{ij}}{8d_{ij}^2} \left(|r_{ij}|^2 - d_{ij}^2 \right)^2 + \sum_{j < k} \frac{3\beta_{ijk}}{8d_{ij}d_{jk}} \left(r_{ij} \cdot r_{jk} + \frac{1}{3}d_{ij}d_{jk} \right)^2 \right]$$
(3.13)

where the coefficients α_{ij} and β_{ijk} are element specific parameters. The variable r_{ij} is the vector between atoms i and j, and d_{ij} is the scalar distance between those two atoms. The Keating potential is unique since the neighbor list is specified such that all atoms have exactly 4 neighbors regardless of the distance to those neighbors. This lends itself naturally to tetrahedral systems that are 4 coordinated but makes it totally unsuitable for studying anything that is not 4 coordinated.

The WWW method begins with a perfect crystal diamond structure. An atom and one of its neighbors are selected at random. These two atoms swap neighbors as is shown in figure 3.15, the structure is then relaxed. The total energy is calculated before (V_b) and after (V_f) the swap/relaxation step is taken. The step is accepted if the metropolis criteria are obeyed; that is if

$$V_f < V_b \quad or \quad P < e^{(V_b - V_f)} / k_B T$$
 (3.14)

where P is some random number between 0 and 1, k_B is Boltzmann's constant and T is the temperature of the system. The temperature is initially chosen to be near the melting point of the material and is slowly lowered every time a move is accepted. This method preserves the four folded nature of the initial structure while attempting to eliminate the periodicity. Detecting whether or not the crystal is completely eliminated is challenging and a constant concern when using WWW structures [75].



Figure 3.15: (a)The WWW method operates by selecting two neighboring tetrahedral units,(b) switching a single neighbor between these two units, and (c) relaxing the resulting structure.

Alternatives to the standard WWW have been developed but produce much the same results. Some start with random initial structures [69] while others integrate extra annealing steps [76] in an attempt to eliminate crystal artifacts. All of these final structures are remarkably similar and often deal in variances of < 1 deg in differences in the angular distribution [77]. The goal in using a WWW type model is to develop a base line to compare the nearly hyperuniform LDA generated through molecular dynamics.

3.8.3 The Hyperuniform Low Density Amorphous Structure

A baseline structure was generated through the WWW method developed by S. von Alfthan [77] with 512 atoms and a Keating potential scaled to the optimal Germanium bond length (2.49\AA) . This structure was then annealed at 250K under NVT conditions in VASP.

The hyperuniformity of the density of the as quenched LDA, annealed LDA and WWW LDA are compared using the low-Q structure factor. The raw structure factor are shown

in figure 3.14. The annealed HULDA (blue) and WWW structure show perfect alignment above 3Å. Below the primary peak the annealed HUDLA structure has a small sub-peak at no other structure contains and whose origin remains unknown. At the low-Q values oscillations due to our fixed volume make it difficult to assess the long wavelength limit of the structure factor.

Applying the shape function from equation 3.8.1 to calculate the structure factor allows us to extrapolate the $Q \rightarrow 0$ limiting case. This extrapolation is shown in figure 3.17. A linear fit is performed over the range L/6 and L/4 as described in reference [72]. The annealed hyperuniform and WWW cases are both linear in this region while the as quenched structure is clearly not linear and has a much higher S(0) value. The hyperuniform and WWW Germanium structures both have structure factors near 0.07 and are equivalent within the error bounds. These S(0) values are comparable to the results for hyperuniform Silicon [72] which found S(0) = 0.035.



Figure 3.16: The structure factor computed using the shape function convoluted with the real part of the fourier transform of the RDF. The change in S(Q) as a function of the volume cutoff in the shape function is shown. Clearly the S(0) value approaches zero as $R \to \infty$.



Figure 3.17: Plot of $S(Q \to 0, R)$ against the inverse of R. The linear fit for each curve is shown as a dashed line. The error on the S(0) value is taken from the variance of the linear fit.

3.9 The HDA-HULDA Transition

Experimentally LDA Germanium is typically formed by atomic vapor deposition [7] and was recently formed, for the first time, by quenching of the liquid phase [55] at higher pressures and then releasing this pressure. These complex formation pathways are necessary because Germanium is a monatomic system and despite access to many metastable states during quenching it is remarkably difficult to achieve the quenching rates necessary to freeze directly into the LDA state. Because of this the transition between HDA and HULDA is important.

The HULDA-HDA transition is studied using the same 0K conjugate gradient stepwise method as for the LDA-HDA transition in section 3.6. The starting structure was the 288 atom hyperuniform structure. In contrast to the LDA-HDA transition the HULDA-HDA transition is not reversible using this method. This is likely due to a short coming of the method, the small sample size and limited dynamics allowed using conjugate gradient relaxation.

Throughout the stepwise compression and expansion the structures were tracked for spontaneous crystallization using the Bond Orientation parameter. Above 16GPa the HDA structure begins to crystallize into βSn . The full results are shown in figure 3.18. An 'eyelet' is visible in the pressure and enthalpy revealing hysteresis induced by an energy barrier. Two energy minima are present corresponding to LDA and HDA structures at 23.5Å^3 and 20.5Å^3 . The process is not reversible since final structure ends up at a different P-V point after a full cycle. The final structure is the highly defected LDA which is indicative of an incomplete structural transition.

This gives us some critical information about the shape of the PEL at low temperatures, the energy between neighboring states for the LDA must be high enough that high temperatures are needed to transition between states. Furthermore if we consider defected zones to be part of the HDA state then energy barriers in the HDA zone must be relatively small and capable of hopping down to the LDA region with little to no barrier in the way.

If the final LDA structure produced here is then annealed at the appropriate temperature range (approximately 600K) the structure relaxes to its hyperuniform configuration.



Figure 3.18: The Pressure (top), Cohesive Energy (middle) and Enthalpy (bottom) plotted against the volume for the 0K HDA-LDA transition of the 288 atom system. The system starts from a hyperuniform state (star), transitions to HDA as compression begins and returns to a generic LDA state as pressure is released. All points are colored by their tetrahedrality, red corresponds to $S_g=1$ and light blue is $S_g=0.6$. The corresponding values for the crystal diamond (red dotted) and βSn (blue dotted) structures are overlaid.

When plotted against volume the enthalpy of the hyperuniform structure is higher than its defected counterpart. This is because the hyperuniform structure has a larger pressurevolume contribution to the total enthalpy. Plotting the enthalpy against pressure, as in figure 3.19, shows that at the same pressure HULDA has a lower enthalpy than LDA.

From this same plot we can infer the transition pressure between HULDA and HDA from the point at which the enthalpies cross. At 0K the transition will occur at 6.4GPa, this is in excellent agreement with experimental results that demonstrate a transition pressure of 6GPa [65] and similar calculations performed using a WWW structure that predict a transition pressure of 5GPa [10].

This same calculation was performed using the defected LDA structure, and a transition pressure of 3GPa was found. The lower transition pressure is explained by the fact that the defected structure exists at a higher enthalpy and contains less of the high energy tetrahedral bonds. All evidence points towards the low density amorphous Germanium structure being hyperuniform.



Figure 3.19: The same data in figure 3.18 plotted against the pressure. The HULDA structure (a) is compressed and transitions to the HDA state (b) after undergoing a pressure collpse. As HDA is expanded it transitions back into the defected LDA state similar to the one formed directly from quencing.

3.10 Electronic Density of States

The electronic density of states for the disordered solid and liquid phases of Germanium were calculated using the 288 atom simulations in VASP. The process for generating the liquid states are discussed in the next chapter.



Figure 3.20: The EDOS for amorphous and liquid Germanium. High density phases are on the left and low density phases on the right. A dotted curve are the results taken from the computational study of Kresse [9]. The DOS is adjusted so the Fermi Energy lays at 0eV.

The high density structures are both metallic in nature as the bands at the Fermi energy are fully occupied. Furthermore the High Density Liquid (HDL) has a very similar structure to the HDA.

The hyperuniform low density structures are extremely close to being semiconducting. The more defected structures, LDA and the Low Density Liquid (LDL), have more occupied bands in the gap at the Fermi Energy. The HULDA (green curve) has only 1 occupied band near the Fermi Energy, because of the smoothing routine necessary to generate these figures



Figure 3.21: The vibrational density of states for amorphous and liquid Germanium. The high and low density phases are presented on the left and right respectively. A comparison with another ab-initio study of amorphous Germanium [10] is presented and shows good agreement for the HDA and LDA phases.

it appears fuller than it actually is.

These results are confirmed by other ab-initio simulation studies [9,64] and experiments on the resistivity of amorphous Germanium [65], which show that the LDA has high resistivity and may be a semiconductor while the high density phases are metallic. No study has yet been able to construct a fully gapped low density structure. Part of this challenges is a short coming of the method used here. It is well documented that the PBE approximation for Germanium produces a crystal that has a filled gap [9] which is contrary to experiment, Germanium is indeed semiconducting in its ground state. This is problem was discussed in detail by Bernstein *et. al.* [78]. They found that the gap in diamond Germanium was occupied by a single band at the Γ point, this error likely persists in the amorphous state. It is necessary to incorporate the corrections described by Bernstein *et. al.* which includes shifting the conduction bands to match the experimental band gap. However experimental electronic density of states data for defected and non-defected glassy structures is currently lacking, so this problem remains open for future work.

3.11 Vibrational Density of States

Vibrations in amorphous solids are assumed to be harmonic in nature, and the Debye model for a harmonic solid demonstrates that the number of states increases quadratically as a function of the frequency, e.g. $g(\omega) \propto \omega^2$. While this holds true at many frequencies in low temperature amorphous solids there is an anomaly present near 2THz. This large bump in the otherwise quadratic curve is known as the Boson Peak which is mostly unexplained phenomenon. Several theories have been put forth to explain the Boson Peak and justify the deviation from the Debye model but none are able to reproduce the exactly.

3.12 Summary

In this chapter we have discussed the structural topology of two amorphous Germanium structures, LDA and HDA. Methods for investigating these structures were introduced and various computational techniques for forming amorphous structures were explored. Quenching from the liquid state resulted in forming pure HDA and LDA phases as well as a mixed state, the phase could be controlled by the size of the simulation block and consequently the density of the material.

The high density amorphous phase was shown to have a low tetrahedrality ($S_g = 0.6$) and a coordination of 6 on average, it is a conductor and contains the boson peak. The low density structure is has a coordination of 4 and a high tetrahedral order parameter on average ($S_g = 0.9$). The transition pressure between the HDA and LDA is was found to be 6.4GPa, in good agreement with experiment.

Depending on the defect density of the LDA phase is either a semi-conductor or a nearly gapped conductor. Fewer defects imply a larger gap in the electronic density of states. The transition to much lower defected state, referred to as HULDA, was found to occur when annealing LDA at 600K. The nature of the hyperuniformity was investigated using the

Torquato criteria for $S(Q \rightarrow 0).$

This study reveals some of the underlying characteristics of the potential energy landscape at low temperatures. We know the barriers between neighboring states for LDA are very high because they require such high temperatures to overcome them. The anneal temperature which activated the structural transition in the LDA was very close to the melting temperature.

Chapter 4: Germanium - Liquid States

4.1 Liquid Polymorphism

In the last chapter it was demonstrated that by quenching Germanium at various densities unique amorphous structures can be formed. The question of whether these structures can exist as unique liquid phases that coincide with unique liquid phases in the PEL as in figure 1.3 is still open. To date there is no conclusive experimental evidence of multiple liquid phases in any tetrahedral network forming liquid.

To date only one experiment has been able to successfully vitrify Germanium into its glassy phase [55]. This was achieved by quenching at high pressures near the minima in the melting curve, quenching, and then releasing the pressure. To help elucidate why this is possible the phase diagram of Germanium is presented in figure 4.1 with a hypothetical Liquid-Liquid phase transition line. Quenching at lower pressures squarely in the Diamond phase stability zone results directly in crystallization, this is because experimental quenching cannot take place fast enough to achieve the glass using current experimental methods. However by quenching at higher pressures near the Diamond- β Sn transition zone there is competition between the two phases during quenching that allows LDA to form. Furthermore in experiment a combination of Diamond crystal and LDA was found, the existence of crystal globules is ancillary evidence of LDL. It is assumed that crystallization is enhanced in LDL because of increased dynamics [55].

Phase diagrams for metastable states are complicated by the time dependence of their stability, complicating the demarcation process. Stability is often a stochastic in nature so the transition lines presented (green dotted/dashed), and while we can calculate pressure and temperature boundaries for a particular state these only imply statistical boundaries beyond which it is more likely one phase exist over the other. For example the 6.4GPa,0K



Figure 4.1: The Germanium phase diagram overlaid with HDL and LDL meta-stability zones. Cooling directly from HDL to LDL is not possible in experiment and involves many complications in simulation.

transition point calculated for the LDA-HDA transition is only the point beyond which HDA is more energetically stable. Experiments have shown HDA can exist at 0GPa if it is cooled to 100K as pressure is released [79]. It was predicted from ab-initio simulations that above 10GPa HDA is the dominant phase [10].

In this chapter we investigate the liquid phases of Germanium through ab-initio simulation. This is a critical study for advancing our knowledge of the metastable liquid phase using one of the few methods that is capable of generating a dynamic tetrahedral state. We begin by presenting details of the HDL and LDL states, including the means by which the LDL state is accessed. A discussion of the fragility of the HDA and LDA states is given and finally the dynamics of the liquid states is investigated.

4.2 Low Density Liquid

Experiments have not been able to directly access the LDL phase in Germanium or Silicon because of several technical challenges. Direct quenches from a high temperature and low pressure zone into the LDL metastability zone results consistently in crystallization [55]. Liquids are remarkably difficult to study *in-situ* because they interact with their



Figure 4.2: Similar to experimental challenges, crystallization occurs in a simulation using the Stillinger-Weber potential when attempting to access the LDL state from HDL. Atoms colored by the Bond Order Parameter (Q_l) with l=3. The crystal seeds present here are red and yellow in color.

environment through surface tension so they are mobile if not properly confined. Magnetic levitation has been applied somewhat successfully to study supercooled HDL [50] and set the lower bound for supercooling (also the upper bound of the LDL zone in figure 4.1). The transition from HDL to LDL is tricky to achieve because it involves high temperatures which result in higher dynamics and broad probing of the PEL, this increases the probability of a crystal seed forming.

Simulations with the Stillinger-Weber potential near the HDL-LDL transition temperature invariably generate crystal seeds forming this is because Stillinger-Weber overestimates the tetrahedral bond energy. The alternative methods of accessing the LDL state is by heating a stable LDA sample slowly enough to enter the LDL stability regime without stumbling into the HDL zone.

Accessing the LDL state using ab-initio simulation is difficult because of the limited efficiency of the calculation makes it hard to identify where the phase is stable. We refer to literature, old simulations and experimental studies to identify the possible stability region. In figure 3.12 quenching and melting simulations are overlaid to this end. At a volume of $24\text{\AA}^3/\text{atom}$ melting occurs from a superheated state above 800K and vitrification sets in



Figure 4.3: The anneal runs (blue and green) are overlaid with 300K hyperuniform structural information.

from a supercooled state at 600K. These are upper and lower existence bounds for LDL. The goal now is to transition from a superheated LDA state to LDL from within these temperature bounds.

Annealing runs at 730K and 770K were performed for 1ns (200,000 time steps). The average RDF and ADF are presented in figure 4.3 along with the Root Mean Squared Displacement (RMSD). The RMSD is the average distance travelled by all of the atoms from their starting location. From this data alone it would be natural to conclude that both samples are glasses not liquids, because the RDFs are nearly identical to the 300K sample as are the angular distributions. The RMSD indicates that for long periods of time (100's of picoseconds) the structure is largely stable and unchanging. The only caveat being towards the end of the 770K anneal, we can see the RMSD suddenly jumps from 2.0Åto 3.2Å. This RMSD is difficult to interpret, it is most flat but with large variances and sudden jumps methods that take into account correlations and individual atomic jumps are needed.

The tetrahedrality and pressure are tracked throughout the simulation. At 730K the

pressure is steady at 1.5 ± 0.5 GPa for the first 0.5ns a slight increase in pressure to 1.6 ± 0.5 GPa occurs over the last 0.5ns. Shifts like this are to be expected as the internal structure of the material transitions from local minima to local minima in the PEL [80]. The tetrahedrality slowly increases in the first 0.25ns of the anneal as the tetrahedrality increases from 0.87 to 0.9, finishing the HULDA shift that started during the 650K anneal. The enthalpy is steady at $-4.05 \pm 0.05 eV/atom$, while the pressure slowly increases from an average of 1.5GPa to 1.7GPa.

At 770K the story is similar but with the higher temperature we see larger structural transitions occurring alongside larger fluctuations. The pressure is now fluctuates between 1.0GPa and 2.0GPa. There is a sudden drop in pressure at the end of the anneal, this coincides with an increase in enthalpy and a decrease in the tetrahedrality. A more indepth analysis of the structure is needed to see if we can link a topological transition to the evolution of the pressure and enthalpy in these anneals.



Figure 4.4: The Pressure, Enthalpy and average Tetrahedrality of the structure during the anneals of 730K (blue) and 770K (green). Extensive units are given in per-atom quantities.

4.2.1 Microstructural Evolution

A close correlation between the pressure and the tetrahedrality can be observed in figure 4.4 and more clearly in figure 4.5. The pressure tends to increase when the tetrahedrality increases, a positive dependence is clearly present.

It should be noted that the tail observed in the 770K anneal (near TOP= 0.84 and Pressure= 0.75GPa) is not necessarily an indication of melting. The material is traversing to a new local minima in which some of the thermal energy is absorbed by dislocating atoms from their tetrahedral arrangement. Whether the trend continues and the material completely melts or if it fluctuates back towards the initial state is a stochastic process and cannot be predetermined from the data taken so far.

Rendering the 3-D structure and coloring by the TOP over time shows spatial correlations in the underlying micro-structure of these low density anneals. At 730K the



Figure 4.5: A positive dependence of the pressure on the tetrahedrality is indicated during the 730K (blue) and 770K (green) is shown here. The solid lines are running averages with a window size of 1000 timesteps, the transparent blobs are the raw data.



Figure 4.6: Top; the atomic structure, colored by tetrahedrality. Atoms with TOP>0.88 are now shown. Bottom; The defect count throughout the anneal at 730K is given.



Figure 4.7: The microstructure is tracked as in figure 4.6.

simulation starts as blobs of low tetrahedrality which are connected by networked strands. The structure appears fractal in nature. Over time defects are annealed out until a single low tetrahedral blob remains. The defect count is defined as the number of atoms with TOP < 0.88. The tetrahedrality presented here is the per-atom average over a window of 1000 time steps. Averaging is used to smooth out high-frequency structural vibrations due to the high temperature. In this 288 atom simulation the defect count drops gradually from 75 atoms to 45 atoms, those defected atoms that remain are clustered together.

A defect clustered about a central point is again observed at 770K. From figure 4.7 the structure is composed of a central blob that 'breathes', growing and shrinking over time. The size of the defect blob fluctuates between 60 and 122 atoms, nearly half of the simulation block. The end of the simulation shows that the defect core does not grow endlessly but is stable at a size of 100 atoms. Further annealing could reveal further transitions expanding the core or shrinking it.

4.3 Dynamics

To better understand the annealed structures and determine whether they are a heated LDA state or actually the LDL state we study their dynamics. The simplest measure of dynamics is the RMSD, which was discussed above and shown in figure 4.3. It is defined as;

$$RMSD(t) = \sqrt{\langle |r_i(t) - r_i(0)|^2 \rangle}$$
(4.1)

where the $\langle \cdots \rangle$ are an ensemble average over all configurations r_i and all times t. The RMSD can tell us how much a structure changes on average from one point in time to another. In a stable liquid phase we expect to see a continuously increasing RMSD, however in a metastable state at low temperatures relaxation does not occur as a continuous process. The RMSD of figure 4.3 contains long flat portions as well as large jumps over short time spans.

From inspection alone we see that during annealing at 730K and 770K many atoms move not through a continuous process but through discrete hops. We delve deeper into these dynamics by studying the correlation functions in time and space, we hope to quantify the change in dynamics that we can identify directly from inspection as in figure 4.8.

Characteristic motions are further identified by tracking the mean square displacement of individual atoms. Many atoms are entirely stable and stay trapped inside local cages during the anneal simulations. However some atoms undergo invidual hops while others continuously hop around in a sort of ballistic pathway. Diagrams like figure 4.9 are helpful for developing a general idea of kind of motion taking place in the sample but do not quantify it.



Figure 4.8: (a) The pathway of an LDL atom over 10,000 timesteps at 770K. (b) The pathway of an HDL atom over 4,000 timesteps at 770K.



Figure 4.9: Selected atomic RMSDs taken from the first nanosecond of the LDL 730K anneal. The top figure shows high active ballistic motion, the middle diagram is atoms that undergo a single hop and the bottom is the most common activity which atoms that are locked in their cage for the duration of the simulation.

4.3.1 Density Correlation - van Hove Function

The van Hove function is a measure of correlations in partile density and flux. It is defined as [68];

$$G(r,t) = \frac{1}{\rho} \left\langle \rho(r,t)\rho(0,0) \right\rangle = \left\langle \frac{1}{N} \sum_{i < N} \sum_{j < N} \delta\left(r - r_j(t) + r_i(0)\right) \right\rangle$$
(4.2)

The left definition gives us some insight into what the van Hove correlation measures, it is a density-density time-correlation, while the right most function is easiest to implement algorithmically.

The van Hove function is conveniently computed as two distinct functions, the self terms where i = j and the distinct terms where $i \neq j$;

$$G(r,t) = G_s(r,t) + G_d(r,t),$$
(4.3)

$$G_s(r,t) = \left\langle \frac{1}{N} \sum_{i < N} \delta(r - r_i(t) + r_i(0)) \right\rangle, \qquad (4.4)$$

$$G_d(r,t) = \left\langle \frac{1}{N} \sum_{i < N} \sum_{j \neq i < N} \delta(r - r_j(t) + r_i(0)) \right\rangle.$$

$$(4.5)$$

The self part of the van Hove function is interpreted as the probability that an atom has moved some distance, r, over a set period of time. The distinct part is considerably more complex to interpret, it is the probability that some other particle occupies a location a distance r from the first particle over a given period of time. Both terms supply time dependent density information so it is sufficient for our needs to only work with the self term, this has the added advantage that the self term is much faster to compute since it is only a single loop of the set of atoms. Since it is a spherically symmetric value it is often normalized by the quantity $4\pi r^2$, this also enhances long range features that might otherwise remain hidden.

The self term of the van Hove function, $G_s(r, t)$, was computed over the range of the RDF



Figure 4.10: The self term of the van Hove function for the 730K (solid) and 770K (dotted) anneals. The time steps are chosen to sample certain key relaxation regimes.



Figure 4.11: The location of the primary peak of the self term of the van Hove function as a function of time. The blue curve is the 730K anneal and green is for the 770K anneal.

 $(0\text{\AA} \le r \le 10\text{\AA})$ and at a range of time values for both annealing runs. In figure 4.10a during the short time scale, ~ 0.1ps, that a single Gaussian distribution is developed around the average atomic cage size. This means that over a short time scale atoms atoms are trapped within a central cage with a fixed radius. This cage effect is observed in crystalline solids and is referred to there as the Debye-Waller factor [81] and is experimentally observable effect of thermally induced vibrations of atoms.

At all time scales 4.10b-e this cage is persistent, but as shown in figure 4.11 we see that the cage is slowly dissipating. As the peak shifts to longer radii it begins to shrink, meaning that over time the probability that an atom will remain in its cage decreases. This is distinctly a property of a liquid because all atoms participate in the relaxation process. In contrast to a glass-liquid mixture or a super heated glass in which only some of the atoms will relax [82].

As the first cage shrinks a secondary Gaussian emerges at long length scales and is visible in 4.11e at 730K. There is a large gap between 1Å and 2Å, the 2nd peak is at 2.7Å, beyond the first peak of the RDF. The dynamics indicate that atoms do not simply hop or swap with their first neighbor but move into the interstitial gaps in between. At 770K in $G_s(r, t = 500ps)$ the 2nd 3rd and 4th peaks are much higher and begin to form a broad secondary distribution that is associated with the dynamics of a liquid. A similar secondary broad distribution is also visible in the 730K $G_s(r, t = 500ps)$ although it is much smaller. In a simple liquid above its melting temperature the $G_s(r, t) \sim 1/V$, the distribution is an ever expanding Gaussian with a width proportional to the t^2 [68]. The broadening of G_s is an indication that at long time scales it is tending towards the dynamics of a typical liquid.

4.3.2 Time Correlations - Intermediate Scattering Function

The van Hove function is a real space quantity, however for a network forming liquid it clearly has some interesting periodic behavior. To that end we apply a spatial Fourier transform to the function to study its behavior in the frequency domain. This is also known analytically as the Intermediate Scattering Function which is defined as;

$$F(k,t) = \frac{1}{N} \left\langle \rho_k(t) \rho_{-k}(0) \right\rangle \tag{4.6}$$

where,

$$\rho_k(t) = \int \rho(r, t) e^{-ik \cdot r} dr$$
(4.7)

and k is a wave vector and ρ_k is the Fourier transform of the real space density ρ . Expanding this function in terms of the van Hove function we have;

$$F(k,t) = \int G(r,t)e^{-ik \cdot r}dr$$
(4.8)

this can further be separated into self and distinct components similar to equation 4.3.1

$$F(k,t) = F_s(k,t) + F_d(k,t)$$
(4.9)

$$F_s(k,t) = \int G_s(r,t)e^{-ik\cdot r}dr \quad \text{and}, \quad F_d(k,t) = \int G_d(r,t)e^{-ik\cdot r}dr \tag{4.10}$$

Again we investigate only the self part of this function, although in testing the distinct and self components look nearly identical. Again the distinct portion is computationally expensive to compute so it is convenient to deem the results superfluous. This is standard practice as inelastic scattering results are only comparable with the self component [68].

When calculating the Intermediate Scattering Function (ISF) the wave vector, k, is selected to be k_{max} , the value at which the structure factor is maximized. The ISF can be calculated at any wave vector but by using k_{max} we know we are investigating the response of the material at a frequency which it is sensitive to. It also helps to use a standard for comparisons in the literature.

The Kohlrausch-Williams-Watts (KWW) method is used to fill in the long time scale

decay of the intermediate scattering function. The KWW method is a result of mode coupling theory [83] and is known as an accurate method for fitting the α and β decays of the ISF [84]. This method is needed because at long time scales data is sparse or not available. For example, to observe the full decay of the ISF at the 730K anneal over 100ns of simulation would be needed, this would require over 10 years of computer time to produce! The KWW fit is achieved through a stretched exponential;

$$ISF_s(t) = A * e^{\left(\frac{-t}{\tau}\right)^{\beta}}$$
(4.11)

where the parameters A, τ and β are fit to the simulation data. All of the ISFs presented here used the KWW fit where appropriate, typically above t > 1 ps.



Figure 4.12: (a)The self intermediate scattering function for 730K and 770K LDL anneals are contrasted against HDL at the same temperature. (b) The raw ISF (black) and kww fit (blue), discussed in the text.

The van Hove function is a probability distribution and without the normalizing factor

 $(4\pi r^2)$ its integral is always 1, so we know that $F_s(0,t) = 1$ is always true. The ISF is the probability that a liquid subjected to a density wave ρ_{-k} at time 0 is in the same state after being subjected to a second density wave ρ_k at time t. F_s is near 1 when the system is correlated and 0 when it is uncorrelated.

In figure 4.12 the self part of the ISF is shown. The HDL curve is provided to contrast the LDL anneals. The HDL is referred to as a simple liquid, it begins correlated and over a short period of time decays and becomes uncorrelated [85]. However the 730K and 770K are network forming liquids with strong caging effects. From the van Hove function we know that both the 730K and 770K structures seem to have liquid characteristics. From the ISF we confirm this behavior as the material approaches a completely uncorrelated state beyond 1ns.

The various stages of the ISF are highlighted in figure 4.12b and the quality of the KWW fit is demonstrated. At times less than 0.05ps a microscopic vibration occurs during which time the structure remains unchanged. During this time the atoms have not vibrated sufficiently to 'feel' the effect of their local cages. This is the region in the van Hove curve in which the first peak is growing. Once the atoms relax and experience their vibrational cages, some will inevitably find a pathway in which they can jump out of these cages. This jumping and re-caging is indicated by the dip in labeled by a star in figure 4.12b at which time the structure regains coherence. The bump that follows it is an artifact of the small simulation, and is eliminated when a larger simulation with more atoms as is confirmed by large semi-empirical simulations [84].

The decay from a perfectly correlated structure to an intermediate plateau is known as β -relaxation [68]. In a glass this plateau is on a macro-time scale of seconds or minutes, in a highly viscous liquid a scale of nano or micro seconds is possible. The alpha decay begins to set in beyond t>10ps but must be completed by the KWW fit because the simulation time scale is too short to access the ergodic limits of the liquid.

By breaking the ISF down into a per atom quantity, as in figure 4.14, we gain a deeper understanding of what is taking place here. Some of the atoms have clearly fully relaxed



Figure 4.13: A graphical representation of α and β relaxation on the PEL.

(towards the blue end of the spectrum) while others are still locked in glassy highly correlated state (red curves). The KWW fit for the minimum and maximum relaxation times are shown in black.x

There is no spatial correlation between the time at which the Boson peak occurs and that atoms location in the simulation. Counter intuitively, atoms within the defected zone do not necessarily become uncorrelated faster than those farther from the defect zone. A weak correlation was found between the derivative of the ISF in the β -regime and the time at which the ISF_s becomes completely uncorrelated. This lack of spatial and temporal correlations tells us that relaxation is a stochastic process. Relaxation cannot be predicted from local structural properties or how an atom is correlated at earlier times.

This result was surprising as it was expected that atoms within the defected zone would decay in a similar fashion to those of the HDL since they share structural characteristics. It is likely that the motion of the defect, its ability to travel slowly through the material and exchange atoms with the more stationary bulk masks any correlations that take place over the entire simulation.

4.3.3 Quantifying Atomic Hopping

The van Hove function and ISF give us a hint to which time the atoms tend to start hopping. Using this knowledge we can gather statistics on which atoms have hopped and



Figure 4.14: Per atom break down of the self part of the ISF. Curves are colored by the time at which their Boson peak occurs, red curves decay later than blue.

have completely relaxed. To this end a custom order parameter is used, referred to here as the windowed RMSD or WRMSD;

$$WRMSD_i(t,\tau) = \sqrt{\langle |r_i(t) - r_i(t-\tau)|^2 \rangle}.$$
(4.12)

This is a per-atom quantity that is large when atomic hopping takes place. By selecting the proper time scale and detecting when the $WRMSD_i$ is greater than the Debye-Waller factor for this glass (the upper bound on the first peak in the van Hove function, 1.5Å) we now have a systematic numerical method for counting and detecting atomic hops in our LDL anneals. Counting takes place by summing the total number of atoms with $WRMSD_i(t, \tau) >$ 1.5Å, results are in figure 4.15.

Distinct dynamics are visible dependent on the size of the hopping window. Hops are rare when $\tau \leq 0.5ps$ no more than 1 hop occurring at a time, often no hops occurring at all. Beyond that, in the range $0.5 \leq \tau \leq 5ps$ the hopping rate significantly increases. The atoms involved in hopping within this window tend to be near the defect zone in the anneals, as


Figure 4.15: Hopping counter with a range of window lengths. Hopping criteria are discussed in the text. Total number of atoms in the simulation is 288.

quantified by the tetrahedral order parameter. This was the short coming in quantifying dynamics from the ISF which is an ensemble average, it misses the correlation between the defected atoms and an increase in hopping frequency. This is because defected atoms that tend to hop more will often hop directly into the bulk and no longer be defected. This is where microscopic quantifications are most useful.

Finally at longer time scales $\tau > 25ps$ we start to see the some of the characteristics observed previously in figures 4.6 or 4.4. In particular the dropping of the TOP at the end of the 770K anneal coincides with an increase of topping at $\tau = 50ps$, further confirming that high frequency hopping and the defected zone are overlapping.

4.3.4 Dynamic Heterogeneity

The splitting of the van-Hove function at a single time scale is an indication of dynamic heterogeneity although it lacks a spatial correlation. An additional requirement for dynamic heterogeneity is that the mobility be localized spatially as well as temporally. Using the WRMSD it is possible to visualize our system labeling each atom by how far it has moved over the window $\tau = 5ps$, a critical relaxation time in which some atoms are known to be



Figure 4.16: Evidence of dynamic heterogeneity is visible from inspection from the 730K ensemble WRMSD (left) and TOP (right) with stationary and highly tetrahedral atoms cropped out. The hot spot seen here has both a low TOP and high mobility.

quite mobile. The zone in which atoms have low tetrahedrality overlaps with the zone of highly mobile atoms as shown in figure 4.3.4.

The dynamic hetero-structure present in covalent or network forming liquids are unique, although it is hard to say exactly what shape or interactions this mobile zones may take from such a small simulation. Stillinger-Weber based simulations done for this work have also confirmed these hot spots exist on the larger scale. The round hotspots shown here are in contrast to the dynamic strings formed in multicomponent Lennard-Jones solids [86].

4.4 The HDL transition

For amorphous structures at high temperatures, melting and crystallization are both stochastic processes [68]. If some small part of the material stumbles into a crystal arrangement this seed can either grow, attracting more high symmetry arrangements, or dissipate depending on the temperature. Crystallization has been observed in a number of simulations in the process of studying amorphous Germanium. These simulations are discarded because crystallization is not reversible and ruins the thermodynamics of the metastable states. Crystal seeds are often difficult to find because they inhabit such a small portion of the simulation that they do not necessarily disturb the ensemble properties such as pressure and enthalpy.

The transition to the HDL phase (melting) is readily apparent as a very sudden collapse into a low pressure (-1.5GPa) low enthalpy state, this is in contrast to the crystal phase which exists at a high pressure (2.5GPa) at this density. The melting process begins when the defected droplet, described in the previous section, grows to the point where it engrosses one dimension and is able to reaches around the periodic boundary conditions and connects back to itself. Once this connection takes place melting is inevitable. The separation of a defected core from itself only occurs if the sample is cooled from its current temperature. Once the defect core connects in one direction it proceeds to expand in the other dimensions until the simulation is completely melted. The HDL transition takes place in under 5 picoseconds.

This reveals a certain shortcoming of these simulations, the simulation box is so small as to induce artificial self-interacting effects. To better understand this process semi-empirical simulations on a larger simulation box were carried out. The process of melting was observed in anneals using the Stillinger-Weber potential in a system with 4096 atoms. This process followed similar stages, except that in this simulation box multiple defects are able to form, each of approximately 100-200 atoms. These defected cores slow grow and attach to each other. The structural characteristics don't precisely match that of DFT simulations, these results provide additional evidence that droplet growth is the nature progression for the HDL transition.

4.5 HDL Structure and Dynamics

The HDL is studied through a sequence of anneals under NVT conditions. The anneals are performed sequentially and the first several thousand time steps are dropped from the analysis so only the structure under its equilibrium condition is analyzed.

As has been previously mentioned the HDL structure has a coordination of between 6 and 8, and a tetrahedrality of 0.6. The tetrahedral order parameter is not useful under



Figure 4.17: The Radial Distribution Function (left) and Angular Distribution Function (right) for HDL at a range of temperatures. The LDL RDF and ADF are provided for comparision, clearly these are unique structures.

these conditions because the coordination is not 4. The structure is revealed through a combination of its RDF and ADF in figure 4.17. The RDF approaches 1 at long length scales. At high temperatures it consists of just 2 peaks, 1 at 2.5Å and a second broader peak near 6.0Å. This broad peak breaks down into the second and third shell peaks as temperature drops.

The ADF seen in figure 4.17 shows that the bond angles are widely distributed with a characteristic peak at 45 degrees and a much broader peak centered around 100 degrees. The breadth of bond angles is common among high temperature liquids which are composed of randomly distributed and weakly bonded geometries.

HDL consists of much longer bonds than the LDL this makes sense because its coordination is also higher, a higher coordination requires that more atoms be packed in nearer to a central atom and one way to do this is extend the bond length. This increase in coordination is also why HDL is denser than LDL despite having longer bonds. The distribution of coordination numbers can be seen in figure 4.18 along with a distribution of the pressure. Two things stand out here, the coordination is relatively stable centered around CN=7.7 at high temperatures but below 1000K it begins to drop abruptly. From



Figure 4.18: A histogram of the coordination number (left) and pressure (right) for HDL anneals.

studying the micro-structure of the material it is clear that this drop is an average drop across the whole substance and not due to, say, the formation of tetrahedral units. As the temperature decreases the coordination sharpens and decreases towards its mean at CN=6. This is in contrast to the pressure which fairly steadily drops from -0.18GPa to -1.31GPa as temperature decreases.

Finally we confirm the dynamics of the substance from the ISF shown in figure 4.19. HDL conforms to the definition of a simple liquid in that its intermediate scattering function decays without plateau directly from 1 to 0 and can be perfectly described by mode coupling theory [83]. The relaxation time of the ISF is captured at 1/e, this is an arbitrary value but within the framework of mode coupling theory any definition of a relaxation time based purely on α decay will show the same temperature dependence [84].

4.6 Summary

A standard dynamics investigation was followed to quantify the spatial and density correlations in the super heated low density amorphous phase of Germanium. This study revealed that this phase is in fact a liquid and follows the typical dynamics of a network forming liquid, as demonstrated by the trends in the van Hove function and the Intermediate Scattering Function.



Figure 4.19: Intermediate Scattering Function of HDL at various temperatures. The inset is the relaxation time at ISF(T)=1/e, these values are highlighted by circles over the ISF in the main plot.

A novel set of analyses were developed to demonstrate the spatial and temporal heterogeneity in the LDL and track its evolution. Hopping was quantified through the windowed RMSD and a comparison of the WRMSD against the average tetrahedrality showed that the LDL does have characteristics of dynamic heterogeneity a property commonly seen in glass forming material. LDL is unique in that is just barely provided enough thermal energy to hop out of local structural minima and thus appears to be extremely similar to its solid counterpart, LDA. An in depth study of its dynamics is necessary to confirm it is a liquid at all.

HDL was shown to conform to the standard of a simple liquid. The structural distribution functions showed it be a unique structure different from LDL in terms of both bond length and bond angles. The coordination number and pressure as a function of temperature showed that both dynamics and structural changes account for compressibility of the material as temperature drops. This study represents the first complete study confirming the existence of multiple liquid phases by demonstrating mobility in any network forming liquid with ab-initio simulation.

Chapter 5: Conclusion

Studies demonstrating that multiple liquid phases exist within monatomic materials have been presented here. While previous instances of LLPT have been shown to be due to a molecular transition [44, 87] we have shown here that the transition is in fact due to network forming behavior. In Cerium a network of right-angle bonds appears in the Ce^{f_0} liquid phase while Germanium shows both tetrahedral and octahedral preferences under different conditions. Liquid dynamics have been confirmed in all phases via experiment or ab-initio simulation. The demonstration of mobility through ab-initio simulation for the low density phase of Germanium reveals that this material is indeed a liquid and demonstrates its underlying dynamics. The prediction of a critical point in the liquid-liquid transition of Cerium is the first of its kind as well since it occurs as a stable transition in the liquid phase.

In studying Cerium two stable liquid phases were found from experimental evidence and then confirmed by simulation. By heating the material above its melting point at various pressures we see direct, strong evidence, of two stable liquid phases [23]. The discovery of a second liquid phase has implications into the formation process of Cerium based glasses and changes the pictures of the Cerium PEL. Cerium's multiple disordered phases may contribute to the phase competition that occurs during quenching which is critical to glass formation.

Simulation based studies are the only effective method currently available for accessing the metastable LDL state of Germanium. The evidence provided from DFT simulation given here demonstrates that the liquid Germanium state is achieved directly from heating the LDA phase. This is valuable evidence which future semi-empirical studies can be measured against and is a critical case study for metastable phases in semiconductors. Both of these materials exhibit distinct electronic behavior and undergo semiconductor to metal transitions as temperature increases. They both exhibit negative melting curves due to the volume difference between the stable crystal and liquid phases.

The study of monatomic liquid and amorphous phases is foundational work and part of a novel area in materials science. As phase diagrams are extended to higher temperatures, pressures and shorter time scales we reveal the complexity possible in homogeneous systems.

5.1 Future Work

Several semiconductors are stable as tetrahedral diamond crystal structure this includes the group 14 elements (C,Si,Ge,Sn,Pb,Fl) as well as in compounds such as Ga-As,H₂0,SiO₂ and Na₂O [88]. The question arises which of these compounds are capable of forming multiple liquid phases, what are the rules that govern the stability of these phases and how are they connected to the material's glass forming ability.

Liquid polymorphism phenomenon is not limited to tetrahedral networks, as was shown in Cerium in which the liquids can be characterized by their unique density and electronic characteristics. Several other studies have revealed liquid polymorphism in monatomic systems such as H,N,Se and Cs [87]. When is liquid polymorphism possible, what conditions are required, can it occur for any system which shows angular dependent or covalent bonding characteristics? Indeed the phase diagram of many elements may be much richer than previously thought and the challenge of finding elements.

To form a holistic theory of liquid-liquid phase transitions it necessary to develop a deep understanding of individual systems. Many of the materials described above lack an effective semi-empirical potential that can accurately describe their metastable phases, and so the most effective tool for simulating their interactions is still DFT.

For these reasons the natural progression of this work is to continue studying individual monatomic systems, particularly those that are already known to exhibit a negative melting curve in dP/dT. New computational methods for improving the scaling properties of DFT are constantly being developed [89] and may prove to be a good alternative to semi-empirical



Figure 5.1: A phase diagram overlaid with which elements exhibit characteristics that are commensurate with liquid polymorphism.

potentials. Faster energy calculations will mean that enhanced sampling techniques will be effective in probing metastable states, a quantified picture of the potential energy landscape is necessary to discern between unstable and metastable states.

Many mysteries remain in the Germanium system, as well the neighboring Silicon system. The question of the existence of a critical point that terminates the HDL-LDL transition is still open [90]. The Stillinger-Weber potential predicts the existence of a LLCP at deeply negtive pressures [91], however this remains unconfirmed and a contentious prediction [92]. An ab-initio study along the lines of the one done here is needed to elucidate the whether a maximum in the HDL-crystal phase occurs.

Appendix A: Computational Methods for Spatial and Frequency Distrubions

A.1 Computational Methods for Spatial and Frequency Distribution Functions

The most direct method for studying the structure of liquids and disordered materials is through distribution functions. Using the coordinates of all the atoms at one time step (as if taken from a snapshot) and some simple math we can evaluate the basic structure of a material and build something that can be effectively compared against experiment.

A.1.1 Radial Distribution Function

The Radial Distribution Function, g(r), is the effective probability of finding a particle in a shell of width dr at a distance r from any other atomic center. Analytically it is defined as;

$$g(r) = \frac{1}{\rho} \langle \sum \delta(\vec{r} - \vec{r_i}) \rangle \tag{A.1}$$

with δ the Dirac delta function. It is a histogram of neighboring atomic distances. A normalization factor is introduced so that in an isotropic liquid the g(r) slowly fades to 1 at long r;

$$g(r) = \frac{1}{4\pi r^2 dr \rho} \langle \sum \delta(\vec{r} - \vec{r_i}) \rangle \tag{A.2}$$

where dr is now the width of the bins in the histogram. One of the numerical considerations to take when calculating g(r) is how to properly apply periodic boundary conditions when looping over atomic site pairs. For a cubic simulation of length L, when r > L/2 then g(r)begins to break down because the pair distance has looped back around on to the central atom, this effect is shown in figure A.1.



Figure A.1: (left) The g(r) circle with r < L/2. (right) When r > L/2 the binning-sphere loops back around on itself and can double count particles.

A.1.2 Structure Factor

The Structure Factor is the Fourier transform of the radial distribution function;

$$S(Q) = 1 + \rho \int (r)e^{i\mathbf{Q}\cdot\mathbf{r}} \text{where}h(r) = g(r) - 1$$
(A.3)

it is also defined directly as

$$S(Q) = \frac{1}{N} \left\langle \sum_{j \neq k} e^{-i\mathbf{Q} \cdot (\mathbf{r_j} - \mathbf{r_k})} \right\rangle$$
(A.4)

The latter function is complete in that it contains all of the S(q) information for Q > 1/Lhowever it is computationally expensive to compute. Although many of the ensembles investigated contain only a couple of hundred atoms it is necessary to average these functions over several thousand configurations resulting in hundreds of billions of functions to evaluate. Thus the latter function is discarded entirely and we focus on computing with equation A.1.2.

Unlike the radial distribution function the structure factor is directly measurable via

experiment through X-Ray diffraction. These functions are composable so the RDF can be uniquely determined from the SF alone. In practice however the standard numerical challenges apply when computing the Fourier Transform; e.g. artifacts are introduced when using a finite source function, and sampling problems such as aliasing can occur when g(r)is not of sufficiently high resolution. The latter is easily over come by using a sufficient number of bins when computing the radial distribution function. The former problem is often not possible to defeat because the radial distribution function is only correct over the range r < L/2 where L is the shortest length of the simulation box. Methods for overcoming this problem are discussed in the main text when it is necessary to solve for the limiting case $Q \to \infty$.

The integral in equation A.1.2 is over all atomic coordinates \mathbf{r} , this is much faster than the integral over atomic pairs (j-k). However there is an implied average over the wave vector Q which is selected on the inverse grid;

$$Q = \frac{2\pi}{L\sqrt{m^2 + n^2 + l^2}}$$
(A.5)

where m, n and l are integers. We can further improve the efficiency of this calculation for isotropic liquids, because the radial distribution function is spherically symmetric the structure factor can be reduced to

$$S(Q) = 1 + 4\pi\rho \int_0^\infty r^2 h(r) \frac{\sin(Qr)}{Qr} dr$$
(A.6)

here Q and r are scalars not vectors. This function is the one evaluated and used in the main text unless otherwise specified. The primary trouble with using this function is the reliance on a smooth and long radial distribution function which is often difficult to ascertain.

A.1.3 Angular Distribution Function

The radial distribution function is a binning of the distance between all pairs of atoms i and j. The angular distribution function is similarly calculated by binning the angle between all atomic triples i,j,k that all lay within the cutoff r_c .

$$g(\theta) = \frac{1}{N^2} \sum_{i \neq j \neq k < N} \delta(\theta(r_i, r_j, r_k))$$
(A.7)

This is often a more desirable function than the tetrahedrality or the bond order parameter because it gives us complete information, however it cannot be broken down on a per-atom basis but is an ensemble average.

Appendix B: Semi-Empirical Potentials

The process of generating semi-empirical potentials is described here. This process is followed in generating the two EAM Ce potentials as well as the Ge ADP potential.

B.1 About Semi-Empirical Potentials

The basic goal of using a semi-empirical potential is to greatly improve the efficiency of MD simulations by eliminating Schrödinger's Equation and simplifying the energy calculations down to a simple pair wise interaction. With an analytical function for the energy based purely on the chemical type of the atoms and their coordinates it is possible to propagate the system using Newton's equation of motion and solving for the force on each atom as;

$$F_i = -\nabla_{r_i} \sum_{j \in neighb_i} V_{ij} \tag{B.1}$$

The total potential energy of such a simplified system is;

$$V_{total} = \sum_{i < N} V_i \tag{B.2}$$

where N is the total number of atoms. The energy of each individual atom is simply the sum of its interactions with neighbouring atoms;

$$V_i = \sum_{j \in neighb_i} V_{ij} \tag{B.3}$$

Generally this is the simplest form a semi-empirical potential can take. The Lennard-Jones[93] and Morse[94] potentials conform to this standard and are often best used for describing simple ballistic systems such as the noble gases. Generally more terms are necessary to describe more complex systems. For instance, semi-conductors which interact covalently generally have a direction preference when bonding. A 3-body term is necessary to describe angular interactions so the single atomic energy would take the form;

$$V_i = \sum_{j \in neighb_i} V_{ij} + \sum_{j \in neighb_i} \sum_{j \neq k \in neighb_i} V_{ijk}$$
(B.4)

Examples of potentials that take this form are the Stillinger-Weber[30] potential and the Tersoff[95] potentials. For other more complex systems with more complex interactions than just angular dependence different potential forms are needed.

B.2 Fitting A Potential

To create a potential we must generate functions that takes as input atomic coordinates and spits out the potential energy for each atom. For example the EAM potential requires that 3 functions be generated, the embedding function F, the pairwise interaction function *phi* and electron density function $\bar{\rho}$. These functions can be represented analytically (e.g. a finite Taylor series) however it is much simpler and often more accurate to describe them as tables of values and use splines for interpolation. The process of developing these system dependent functions is referred to as fitting.

The most important part of the fitting process is generating an accurate picture of the PEL in regions of interest. To this end a large database of relevant configurations including atomic coordinates, forces, total stresses and total energy are used. These configurations are generated through high fidelity DFT calculations which produce the atomic forces, stresses and energies given a set of atomic coordinates. The coordinates of an atomic system tell us where in the PEL we are where as the energy, forces and other system dependent quantities tell us the shape of the PEL at that point.

An optimization routine is employed to minimize the error that the model potential produces when replicating the database structures and parameters. The optimization process was performed using the code "POTFIT" [96] which natively supports several analytical and tabular potentials. Weights for each of the configurations are applied, this ensures that more common structures such as the ground state, are fit with a greater importance than less common or unstable configurations. We can tell POTFIT what optimization routine to use, what potential form to use and provide it with our database of structures, weights, and empirical information it then attempts to minimize the error function. An example of an error function is;

$$Error = \sum_{c < M} \left[w_c^E (E_c^{db} - E_c^{pot})^2 + w_c^F \sum_{i \in c} (F_i^{db} - F_i^{pot})^2 + \sum_{d < 6} w_c^S (S_d^{db} - S_d^{pot})^2 \right] + \sum_{sed} A_{sed}^{lit} - A_{sed}^{pot})^2$$
(B.5)

The first two terms are contributions from total energy and per atom forces multiplied by their corresponding weights. The 3rd term is the contribution of the pressure or direction stress (6 directions include xx, yy, zz, xy, xz, and yz). The last term is the contribution from empirical values A, such as the defect energies, surface energies, elastic constants or phonon dispersion curves. All of these values were not included by default in POTFIT so it was necessary to develop the code to support these kinds of operations. Terms labelled with dbare database values, where as terms with *pot* are this current iteration's computed potential values.

As mentioned above the fitting process consists of minimizing equation B.5 which is a function of hundreds of variables. This is a challenging process with no direct solution, the best we can do is use a global optimization routine and hope that our starting parameters are close enough to a valid solution that something useful comes out. POTFIT provides us with two global optimizers, a Genetic Algorithm and Simulated Annealing. It was found through several trial runs that Simulated Annealing is often able to find a sufficiently useful minima with little tuning; in contrast to the Genetic Algorithm which was inconsistent and required significant tuning.

There are several variations on the fitting process used to enhance the finished potential. It is possible to include experimental data directly into the fitting process by altering the error function to calculate and include the discrepancies of the empirical value[97], this is the 4th term in equation B.5. Also, since DFT introduces systematic errors in optimal bond length a transformation can be applied to attempt to bring the DFT PEL closer to the empirical (real) PEL. The scaling functions are

$$X' = X * A$$

$$E' = E * B - C$$

$$F' = F * B/A$$

$$S' = S * B/A^{3}$$
(B.6)

where X is atomic positions, E is total energy, F is force per atom and S is total stress. The constants A, B, C are derived by obtaining the equilibrium energy and volume of the ground state produced by the potential, as well as its melting point. From there the parameters A and C are calculated directly, while B is adjusted manually to ensure an appropriate melting temperature. The database of configurations is adjusted accordingly before fitting takes place.

Tests ensure the quality of the final potential. Some common tests include defect energy comparisons, elastic constants, phonon dispersion curve calculations, melting temperature, Bulk and Young's modulus and thermal expansion coefficients. If any of these tests show that the calculated property significantly differs from literature, more configurations that are relevant to the property of interest are added to the database and weightings are readjusted. This process of correcting macroscopic properties can often be tricky and requires some intuition into the nature of the configurations that affect a particular property.

B.3 Semi-Empirical Germanium Potentials

Before any computational materials study can be started an appropriate simulation method must be selected. Because the primary concerns of the study of Germanium lay with an accurate description of its structure and time dependent dynamics but not its electronic configuration the first method explored were semi-empirical which treat the atoms as point particles and do not contain any electrons. There are several semi-empirical potentials available for Germanium already in literature and their behavior is explored here.

All tests were performed on NPT systems with 512 atoms and a time step of 5fs. The starting cF8 diamond crystal phase was heated to 2500K unless necessary to go higher, and quenched to 100K. From there the systems were heated to 2500K to inspect the LDA, LDL and HDL phase characteristics.

B.3.1 Stillinger-Weber Germanium

Stillinger Weber type potentials were designed to study various aspects of materials with Tetrahedral ordering or a Diamond crystal ground state. These all take the form of;

$$E = \sum_{j>i} \left(\phi_2(r_{ij}) + \sum_{k>j} \phi_3(r_{ij}, r_{ik}, r_{jk}) \right)$$
(B.7)

$$\phi_2(r_{ij}) = A\epsilon \left[B\left(\frac{\sigma}{r_{ij}}\right)^p - \left(\frac{\sigma}{r_{ij}}\right)^q \right] e^{\frac{\sigma}{r_{ij} - a\sigma}}$$
(B.8)

$$\phi_3(r_{ij}, r_{ik}, r_{jk}) = \lambda \epsilon_2 \left[\cos\theta_{ijk} - \cos\theta_0 \right]^2 e^{\frac{\gamma\sigma}{r_{ij} - a\sigma}} e^{\frac{\gamma\sigma}{r_{ik} - a\sigma}}$$
(B.9)

Several user parameters are used including, $A, B, p, q, \sigma, \lambda, \epsilon, \theta_0$, and γ . Most of these parameters are borrowed from the enormously popular Stillinger-Weber potential for Silicon[30]. These potentials are composed of two components, a pair wise additive force (ϕ_2) which is dominant in the HDL phase, and an angular term (ϕ_3) which is dominant in the low density highly tetrahedral phases. Each potential have unique values for key coefficients, in particular λ and σ which determine the angular and pair-wise contribution, respectively.

Table B.1:	Stillinger-Weber	Si potential.
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ϵ	σ	a	λ	γ	$cos heta_0$	А	В	р	q
2.1863	2.0951	1.80	21.0	1.20	-1/3	7.0496	0.6022	4.0	0

Table B.2: Stillinger-Weber type Ge potentials. All values not given are taken from Stillinger Weber Silicon in table B.3.1.

Potential	Parameters
Ding[98]	$\epsilon = 1.93, \sigma = 2.181, \lambda = 31.0$
Mod-Ding[99]	$\epsilon = 1.58, \sigma = 2.181$
Jian[100]	$\epsilon = 1.93, \sigma = 2.181, \lambda = 8.37, A = 6.769, B = 0.6166$
YuIII[101]	$\epsilon = 1.66, \sigma = 2.215$

The Silicon potential is a good starting point for Germanium because their phase diagrams are so similar and their liquid and amorphous phases are similar in structure.

The Ding potential[98] is unique because it has an increased tetrahedral contribution with $\lambda = 31$, this is useful in generating the HULDA structure however it significantly increases the odds of crystal seed formation. In addition it was not possible to produce the HDA phase using this potential.

Nordlund[99] attempted to correct for this by decreasing the angular contribution and adjusting the pair-wise contribution to make the material melt closer to the experimental melting point of Germanium. The amorphous phases of this material are erroneous and do not in any way match the LDA or HDA phases of Germanium.

The Jian[100] potential was designed to correctly produce the phonon-dispersion curves of Germanium, and while it does correctly reproduce the vibrational behavior of Germanium the crystal phase above 300K was found to be unstable. The βSn structure was found to be more energetically stable at nearly all temperatures.

Yu[101] produced 3 potentials with the goal of studying the diffusivity of Germanium and Silicon defects in liquid Germanium. All 3 potentials were chosen so that the melting point matches that of empirical results (1211K) and they all produce a good liquid structure. However none of these potentials an produce an accurate quenched structure.

All of these potentials have applications in which they are appropriate, however none of them are capable of capturing the transition between high density and low density phases. Furthermore Stilling-Weber potentials are known for under estimating the diffusivity of the liquid phase because they tend towards longer range tetrahedral ordering[101].

B.3.2 Tersoff Germanium

The Tersoff potential is defined [95];

$$E = \sum_{j>i} 2f_c(r_{ij}) \left[a_{ij} A e^{-\lambda_1 r_{ij}} - b_{ij} B e^{\lambda_2 r_{ij}} \right]$$
(B.10)
$$f_c(r < R - D) = 1, \quad f_c(r > R + D) = 0,$$

$$f_c(R - D < r < R + D) = \frac{1}{2} - \frac{1}{2} sin \left(\frac{\pi}{2} (r - R) / D \right)$$

For the full definition of all of the terms readers are referred to [95]. The potential was developed to fit empirical data of covalent systems. It has several shortcomings for the Germanium system. The melting temperature is 2700K, more than double the empirical value, the liquid structure and glass structures do not match experiment.

B.3.3 Modified-EAM Germanium

The Modified EAM potential or MEAM takes many different forms according to the system it is describing. It was first defined by Baskes[102] to enhance the embedded atom method to include an angle dependent electron density. While it was first used to describe the Silicon system under shear stress it was further extended to 20 other monatomic cubic systems[103] and then further refined for several other FCC alloys[104]. A promising MEAM potential refined by Kim[105], which reproduces many features of the equation of state. However it was found that while the glass structure is very close to the DFT results available in literature[60], it contains approximately 5% anomalous bounds at 75°, these bonds are overly soft and overly enhance the dynamics of the glass as it is heated. This would defeat any study of the low density liquid phase which has dynamics that are highly sensitive to temperature.

B.3.4 Summary of Semi-Empirical Germanium Potentials

Several semi-empirical potentials were investigated for studying the liquid and amorphous phases of Germanium. While many of these reproduce one aspect of the disordered material (for example most potentials and produce a good approximation to the LDA structure), none of them are capable of capturing the dynamics of LDL phase and a transition from the LDA to the HDA phase. Lee's efforts to modify the MEAM potential so that it can properly describe the dynamics metastable network forming liquids are on-going and this work seems promising.

As part of this work an Angular Dependent Potential[106] was developed but similar short-comings to that of MEAM were found. Two challenges arise when developing a potential for describing tetrahedral networked materials. The potential must be able to describe accurately the energy and dominance of two different disordered materials, one with tetrahedral (LDA) preference and the other with octahedral (HDA) ordering. The transition between these two phases requires a different kind of dynamics from that of the transition from LDA and LDL. This is assumed to be due to the deficiency of the fitting process which relies on fitting static properties (ensemble energy, inter-atomic forces, etc) instead of dynamic parameters. For example, it would be extremely difficult to develop a computationally efficient fitting process that enforces a fit to the RMSD of a material.

The effort to develop a new potential for Germanium was abandoned because of these short comings and using direct DFT simulations was chosen instead. There are several advantages in using ab-initio simulations, the foremost being that it is able to correctly reproduce and even predict the dynamics and phase transition mechanics of many amorphous materials.

Appendix C: Thermodynamic Integration

look this up in textbook Understanding Molecular Simulation, Second Edition: From Algorithms to Applications and re-write it

The Gibbs free energy of the two phase liquid Cerium system is evaluated individually using Thermodynamic Integration. The idea

In the first step, we switch the liquid under the constant volume and constant temperature condition to an intermediate reference system, which is a collection of particles interacting through a repulsive Gaussian type pair potential with the following form

$$\Phi = Ae^{\left(\frac{-B}{r^2}\right)} \tag{C.1}$$

where A and B are two model parameters (A=13.8eV and B=0.25) are used in this work. The selection of the Gaussian potential is to avoid crossing any phase transition line during thermodynamic integration. During the switch, the system has the following potential energy function:

$$E = (1 - \lambda)U_{EAM} + \lambda\Phi \tag{C.2}$$

where λ is a switching parameter varying from 0 to 1 and U is the EAM potential energy. The Helmholtz free energy change during this step is given by

$$\delta f_1 = \int_0^1 d\lambda \langle U - \Phi \rangle_\lambda \tag{C.3}$$

the $\langle \rangle_{\lambda}$ is the ensemble average.

In the second step, the Gaussian potential is gradually switched off and the intermediate reference liquid is eventually switched to an ideal gas. The system during the switch has the potential energy function $E = \lambda \Phi$. The Helmholtz free energy change during this step is given by

$$\delta f_2 = \int_0^1 d\lambda \langle \Phi \rangle_\lambda \tag{C.4}$$

The liquid Gibbs free energy is given by

$$g(T_0, P_0) = \delta f_1 + \delta f_2 + f_{id}(T_0, V_0) + P_0 V_0 \tag{C.5}$$

where $f_{id}(T_0, V_0)$ is the Helmholtz free energy of the ideal gas and

$$f_{id}(T_0, V_0) = k_B T_0 \left[ln(p\Lambda^3) - 1 \right]$$
 (C.6)

where k_B is the Boltzmann constant, ρ is the number density of the system and Λ is

$$\Lambda = h / \sqrt{2\pi m k_B T_0} \tag{C.7}$$

is the thermal de Broglie wavelength. The Gibbs free energy of liquid Ce at any given temperature and pressure g(T, P), can thus be derived from $g(T_0, P_0)$ via isobar and isothermal thermodynamic integration paths employing the following two thermodynamic relations.

$$g(T_0, P) = g(T_0, P_0) + \int_{p_0}^p V(T_0, p) dp$$
(C.8)

$$\frac{g(T,P)}{T} - \frac{g(T_0,P)}{T_0} = -\int_{T_0}^T \frac{H(\tau,P)}{\tau^2} d\tau$$
(C.9)

where H is the enthalpy of the system.

Appendix D: Description of Software

A large code base was developed for carrying out the calculations described above. All code developed as a part of this thesis is available online at;

https://github.com/acadien/matcalc

A basic description of the tool set is provided here. All code is written in python and requires the use of the Numpy, Scipy, Matplotlib and Qhull libraries.

The analysis package contains code meant to be imported;

- datatools.py, structtools.py sf.py, rdf.py all contain functions for doing math on datasets.
- orderParam.py contains a set of abstractions for calling order parameters on datasets, these have all been highly optimized, this is the preferred method for calling order parameter functions such as tetrahedrality.
- ensemble (Function) packages compute the per atom quantities over a configuration file and dump them to a new file.
- neighbors.py contains functions for working with and computing neighbor lists.

The diffusion packages contains a set of functions for computing dynamic quantities and correlation functions.

- ISF.py, vanHove.py and stressAutoCorrelate.py compute the correlation functions on a set of atomic coordinates provided by an OUTCAR file.
- kwwfit.py applies the KWW algorithm to the computed ISF.
- rmsdAnalysis.py and hopAnalysis.py are slow functions that compute hopping parameters.
- dynSus.py computes the dynamics susceptibility of intermediate scattering function, just a Fourier transform.

Other packages are for file IO with specific compute packages, such as the vasp, siesta and moldyn packages. The plotremote package is a collection of tools for working effectively remotely, useful for dumping plots to network drives.

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Biography

Adam S. Cadien graduated from Sunset High school in Portland, Oregon in 2003. He received his Bachelor of Science from the University of British Colombia in 2008. As an undergraduate he worked as a research assistant in the Physics Department and held internships as a software developer at Lumerical Inc., at CERN's Large Hadron Collider and Abound Logic. He went on to complete his Masters of Science in 2012 at George Mason University where he worked as a graduate research assistant and lecturer. He received awards as an outstanding student and top graduate lecturer.