Order Within Disorder: Theory and Simulation of Amorphous and Carbonaceous Materials

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This dissertation titled

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Abstract

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Despite the long standing history of the research, production, and application of amorphous and glassy materials, generating good quality models still remains a challenge. The challenge arises from the inherent lack of the long range order, characteristic of crystals, in amorphous materials. Researchers have developed various techniques to create models of amorphous materials ranging from random Monte Carlo to classical molecular dynamics and from *ab initio* to the most recent machine-learned methods. In this dissertation, we apply force enhanced atomic refinement (FEAR) whereby experimental information from diffraction measurements are used jointly with *ab initio* density functional theory (DFT) based energy minimization to produce models of various amorphous materials that agree with diffraction data and are a suitable energy minimum of the chosen interatomic potential functions. By generating models of metal oxides and chalcogenides, we show that this method is broadly applicable to amorphous material if the experimental diffraction data is available. We used this to study the annealing induced changes in the structure of ZrO_2 -Ta₂O₅, a potential candidate for mirror coatings for the Laser Interferometer Gravitational-wave Observatory (LIGO) interferometer mirrors. We find that annealing increases the fraction of corner-shared metal-oxygen polyhedra in this material. Motivated by interest in carbonaceous materials, we studied the graphitization of carbon at temperatures near 3000 K. For the first time, we accurately simulate the process of graphitization and the mechanisms of layering. We have seen that individual layers of amorphous graphite are topologically disordered with some pentagon and heptagon

carbon rings and have studied the effects of this disorder on charge density distribution, electronic density of states, and electronic conduction. The study of carbonaceous materials was extended to study the reactivity of carbon surfaces to different atmospheric gases. To gain a better insight into the structure of the carbon foams, we developed a foaming algorithm and studied the dependence of porosity, density, and pore radius on the fraction of different hybridization using machine-learned interatomic potentials.

DEDICATION

Dedicated to my dad, Ramesh Kumar Thapa, who could not witness this adventure.

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LIST OF ACRONYMS

BMG	Bulk Metallic Glasses
SPC	Space Projected Conductivity
DoS	Density of States
IPR	Inverse Participation Ratio
LDA	Local Density Approximation.
GGA	Generalized Gradient Approximation
PAW	Projector Augmented Wave
FPMD	First Principles Molecular Dynamics
RMC	Reverse Monte Carlo
FEAR	Force Enhanced Atomic Refinement
VASP	Vienna ab initio Simulation Package
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
ML	Machine Learning
GAP	Gaussian Approximation Potential
CBRAM	Conducting Bridge Random Access Memory

1 INTRODUCTION

1.1 Background and Survey of the Thesis

Amorphous and glassy materials have wide application and thus attract vast research interest. Since these materials lack long range periodicity, characteristic of crystals, the understanding of the structure is challenging. For crystals, structural characterization is relatively easy with diffraction experiments because crystalline order manifests as sharp intensity Bragg peaks at well-defined locations. However, the lack of such periodicity in amorphous materials produces broad peaks, making the characterization less subtle. Having said that, one should take care to not think of amorphous materials as having a random arrangements of atoms as in gases. They always have a well defined short range order (usually up to 5 Å).

Carbonaceous materials appear everywhere in nature: from the human body to plants and from coal to diamond. The ability of carbon atoms to be bonded with different coordination is the main reason behind the incredible variation manifested by carbon materials. Carbon materials have widespread applications ranging from Lithium-ion battery anodes to jewelry and from wall siding materials to nuclear reactors. Recently, the green use of coal has attracted a lot of interest. One such application is the practical utilization of carbon foam.

The principal focus in this thesis involves simulating models of various amorphous and carbonaceous materials of scientific and industrial importance. We have studied amorphous carbon over a wide range of density using *ab initio* MD as well as machine-learned interatomic potentials [5, 6]. The machine learned potentials offered *linear scaling* of computer time with system size and gave us the liberty to work with large models with accuracy close to DFT level. Using *ab initio* MD and machine-learned techniques, we studied the structural transformation of non-crystalline carbon in a certain density window into amorphous graphite. We have used MD simulation to understand the structure and properties of carbon surfaces and their reactivity to different atmospheric gases. We used ML potentials to make models of carbon foams using a foaming algorithm developed in the course of this dissertation.

FEAR was used to study subtle changes in the structure and thereby properties of interest arising from annealing induced effects on a potential mirror coating on LIGO interferometer mirrors [7]. In addition to that, FEAR was used to study the GeSe glasses in the intermediate range [8].

The rest of the sections in this chapter has been coauthored by D. A. Drabold, and R. Thapa and published as *Thapa, R. and Drabold, D. A.* (2022), *Ab initio* Simulation of Amorphous Materials, in Atomistic Simulations of Glasses (eds J. Du and A. N. Cormack) [9].

1.2 Big Picture

Experiments determine our state of knowledge about the physical world, and come in all shapes and sizes. Diffraction of X-rays, neutrons or electrons convey essential information about local ordering of atoms, EXAFS gives specific information about local structural order derived from the electronic structure of the system. The electronic density of states can be indirectly measured by photoemission experiments or inferred from optical absorption. The electronic tail states are built from valence and conduction states near the Fermi level and are the key to doping, transport and optics. The vibrations of the network are essential to understanding thermal and mechanical properties.

We argue then, that to understand disordered phases of condensed matter, a full set of experiments and realistic computer models are required. Naturally, obtaining "convergence" between experiments and theory is necessary and can sometimes be an iterative process. As a point of logic, the more experiments we have, the more information we possess about the material. The information intrinsic to a neutron diffraction experiment is very different than a measurement of optical absorption or v ibrations. In principle, as each new experiment is performed, we should create models anew to jointly satisfy *all* the experiments. And it is not uncommon to find that one experiment is relatively "easy" to represent and others might be quite difficult. We show that usually highly accurate "*ab initio*" interatomic interactions are required for these complex systems.

1.3 The Limits of Experiment

1.3.1 The Scourge of Averaging

Most measurements on materials involve macroscopic numbers of atoms, and thus are an average over myriad local environments, hence the smoothing (compared to crystals) of measured observables. Local probes of materials are important and are especially relevant to amorphous materials if the spatial resolution of the experiment is fine enough to detect variation in local e nvironments. Perhaps the ultimate example of a local probe is atomic resolution scanning tunneling microscopy (STM). Techniques like micro Raman can probe materials on a *ca*.1 micron length scale. Obviously enough, all "spectroscopic" techniques face related challenges: to get a measurable spin-resonance, Raman, IR... signal, many atoms are needed to enable the measurement, and the signal is necessarily averaged over these. Electronic and transport measurements suffer analogously. So for disordered systems, experiments do not usually offer direct information about atomic scale disorder, but instead provide "sum rules" (structural, electronic, and otherwise) that a good computer model must satisfy.

1.3.2 Diffraction

For crystals it is usually possible to "invert" the structure from diffraction measurements. The intuitive reason is that the information contained in a palisade of Bragg peaks [10] is vast – mathematically speaking it is approximately a collection of Dirac δ functions with intensity and energy precisely defined. By contrast, the diffraction structure factor S(q) (or the pair-correlation function g(r)) is smooth and the information is commensurately reduced. For sufficiently large distances in space, g(r) asymptotically approaches unity, implying no further structural information. Protein crystallography is one of the great triumphs of modern science, with more than 100,000 entries in the Protein Database and 20 Nobel Prizes [11]. Yet this glittering success depends entirely on the incredible possibility of crystallizing the proteins, and thus cannot help us with our non-crystalline systems.

Diffraction data provides only pair correlations, and it is also blind to chemical order: only the total structure factor is usually measured, so that in a material with (say) two atomic species, we get information about all pair distances with no chemical specificity. The clever and successful method of isotopic substitution [1] of Salmon's group at Bath exploits the fact that neutron scattering lengths can depend strongly on the particular isotope present and thus enables the extraction of partial pair correlations. The method is an important advance, but is not always readily applied to arbitrary materials (since it depends on the availability of possibly rare isotopes to fabricate samples large enough to produce high quality diffraction data). Satisfying diffraction data is necessary but certainly *not* sufficient to guarantee that a computer model is realistic.

1.3.3 Spectroscopic Information

A wide variety of spectroscopic experiments are available and provide valuable information about materials. Meaningful comparisons with models require accurate computations of the electronic, optical and possibly vibrational properties of the computer models. And of course spectroscopic methods are subject to the scourge of averaging!

1.4 Synergy between Experiment and Modeling

Disordered materials are a classic arena for the interplay between experiment, theory and simulation. While we have criticized the limitations of information carried by experiment, there are serious limitations in modeling too (systems so small that they are not obviously physically relevant or adequately sampling the local bonding environments – the opposite of the "averaging" charge lodged above against experiments), inaccuracies in atomic interactions, basic challenges to computing physical observables reliably (as for example accurately computing an optical spectrum), simulation times that are many orders of magnitude removed from all but the fastest spectroscopies. We face a difficult limit: we need accurate interactions, large systems and often extended (say nanosecond) simulation time or a thorough exploration of configuration space that will sample representative local structures. Every "computational knob" should be on maximum for these calculations.

Thus, the respective warts of the experiment and modeling paradigms are limited in opposite ways and if we can bridge the gap between them, then we can gain new and reliable insight into these materials and learn about the limitations of the methods themselves [12].

1.5 History of Simulations and the Need for *ab initio* Methods

The first recognizable MD simulation was carried out by a Swedish astronomer, Erik Holmberg during the second World War [13]. He took advantage of the identical radial r^{-2} dependence of the light intensity with distance from a point source, and the gravitational force to enable simulations based upon an "optical analogy" of the gravitational interaction. Holmberg constructed a clever apparatus in which two groups of 37 lamps each (each lamp representing a star, each group representing a galaxy) interacted optically,

and the light intensity at each lamp ("star") was measured with selenium photocells. Since the light intensity was proportional to the interstellar forces, the time evolution of a galactic collision could then be simulated, and Holmberg was able to see spiral arms and draw inferences about galactic scattering and capture probability.

Early simulations of liquids and materials used *ad hoc* potentials and moved atoms according to classical mechanics (Newton's second law). The primitive computers (and smart scientists) of the time could directly simulate the dynamics of systems with hundreds or thousands of atoms or molecules [14]. While the potentials were crude by modern standards, an impressive amount was learned, and the experience gained with empirical potentials with integration methods, size artifacts, alternate "ensembles" (meaning simulations with different fixed thermodynamic variables) and many other aspects of simulation transferred immediately to the *ab initio* simulations we emphasize here. A classic work in this area is the book of Allen and Tildesley [15].

The first MD simulations used empirical potentials: functions made up to mimic some known behavior about a material. Such a potential might be designed to reproduce the right ground state crystal structure, melting points etc. The trick for such calculations is applying the potential to a structure with different local bonding – as for example carrying out a simulation for an amorphous solid or say a small molecule for a potential that was designed to fit a crystal. Such simulations are hit or miss, and often fail qualitatively. A potential that works in all salient bonding environments is called "transferable". Transferability is impossible to obtain with simple potentials with directional covalent bonding.

Why is it so difficult to make a generally reliable interatomic potential? The answer is short: *electrons*. Consider the ground state conformations for a series of small Si molecules: Si_2 , Si_3 , Si_4 ... Start with a pair of Si atoms. Pair interactions are obviously adequate, and the ground state separation between the atoms is at the minimum in the pair potential energy function $V_2(\mathbf{x_1}, \mathbf{x_2})$ for the dimer. Now add a third atom in the vicinity of the pair. To minimize the energy of the trimer, covalent bonds form between all three atoms (and it turns out the minimum energy configuration is an isoceles triangle with an apex angle of about 80 degree [16]). Note that the presence of atom 3 changes the *pair* interactions – a different V_2 function is required depending on the position of atom 3 ($\mathbf{x_3}$). From elementary chemistry, new linear combinations of the s and p orbitals on all three atoms emerge depending on the positions of all three atoms, so the pair potential picture fails and it is obvious that at least triplet interactions are required $V_3(\mathbf{x_1}, \mathbf{x_2}, \mathbf{x_3})$. This argument can be extended *mutatis mutandis* by adding more and more atoms. In practice for accurate computations, approach fails for practical cluster sizes.

The epiphany needed to break out of this scheme was to admit and treat the origin of the complexity: the electronic structure of the system. The first generation of such methods used single-particle Linear Combination of Atomic Orbitals "tight-binding" recipes for the electronic structure¹. The earliest such calculations used simplified forms for total energies derived from recursion [18] or moment expansions [19, 20] of local electronic densities of states. Soon thereafter, full diagonalization methods were used to compute total energies, for which the electronic component of the total energy came from summing up the electronic eigenvalues of the tight-binding Hamitonian up to the Fermi level, and a balancing repulsive interaction between nuclei was added to obtain a total energy (the potential energy of the configuration). If we think of this "tight-binding total energy functional", it is clear that it is capable of representing much more complex and spatially non-local behavior than an empirical potential. Sankey and Allen [21] were the first to implement this in 1985, now what we call "tight-binding MD". So even though the

¹ The tight-binding models themselves were "empirical", and required extensive fitting to a variety of experiments that limit their transferability. One should never underestimate the insights possible for thoughtful tight-binding calculations, see the classic work of Harrison [17].

tight-binding Hamiltonians of the time were imperfect, the work was a great advance since many of the "electronic structure" aspects of the computation were correctly handled.

Ab initio of course means "from the beginning". This is basically ill-defined, since the *beginning* is subjective. Our purist friends down the hall might want us to start with quarks. What it means in practice is a parameter-free approach to computing the electronic ground state energy and associated quantities like forces. Parameter free means no experiments are fit to, and the prescription for the electronic structure and computation of total energy derives from a general theory of an inhomogeneous electron gas as in a solid or molecule (or in principle, but rarely in practice, many-body wavefunctions).

At about the same time as Sankey and Allen, Car and Parrinello [22] did the first calculations adopting the fundamentally appealing approach of using density functional theory to compute total energies and forces. This was the first truly *ab initio* simulation, and the *ab initio* schemes in wide use today are remote descendants of this fundamental work, and where the local orbital methods are concerned also the work of Allen and Sankey. All of these methods assume the Born-Oppenheimer [23] approximation (separating the ionic and electronic degrees of freedom) and the additional approximation of classical mechanics for ionic motion.

We should also comment that there is a wider world than just MD simulations. Direct MD is sorely limited by the tiny time step (of order 1 fs $(10^{-15}s)$) to correctly integrate the classical equations of motion. A very important problem is the effective exploration of configuration space for a complex system. Various "energy landscape" methods are now in common use including some with *ab initio* interactions [12].

1.6 Ingredients of DFT

A few remarks about DFT is now presented. Drabold has written at least two such summaries [24, 25]. We will largely eschew this task in this dissertation, since there are many masterful treatments available. The historically significant Nobel lecture of Kohn [26] is easily readable. Richard M. Martin [23] has written the gold standard treatment of DFT and *many* important developments that have arisen in the last 20-30 years. The best recent history from another acknowledged master is the recent paper in Reviews of Modern Physics by R. O. Jones [27], who among other things pointed out Dirac's prescient grasp of the concept of DFT prior to 1930.

Still, to make this dissertation somewhat self contained, we will tersely summarize the basic ideas of DFT and leave the equations to Martin and Jones. Hohenberg and Kohn [28] showed that the electronic density was a suitable function from which to exactly compute the ground state energy $E = E(\rho(\mathbf{r}))$ of any inhomogeneous electron gas, that there was a universal functional for the energy of the gas, and provided the variational principle to determine $E(\rho)$ on the road toward practical methods. The primacy of this one scalar field $\rho(\mathbf{r})$, rather than an unimaginably complex many-electron wave function² was profound both philosophically (e.g., to give a better way to "think" about such problems), and also practically, because it led to methods that are readily handled by modern computers. The method was made practical by Kohn and Sham [29], who converted the Hohenberg-Kohn theorem into an effective single-particle problem with a complicated mean or "self-consistent" field in the spirit of the Hartree [30] or Hartree-Fock approximation [31]. The form of the "Kohn-Sham Hamiltonian" is only approximately known, and relies on accurate quantum Monte Carlo calculations on the homogeneous electron gas [32]. The complicated single-particle problem is then solved on some basis set, most commonly plane waves or local orbitals. With the Kohn-Sham eigenvalues and orbitals available, it is easy to compute the single particle density matrix, total energies, forces and indeed many other properties. Such computations typically scale at best with the cube of the number of electrons, so become computationally expensive fast. Attempts

² Kohn argues that it does not make sense to even try to compute many-electron wavefunctions if the number of electrons exceeds about 100 [26].

to improve the scaling have been somewhat successful, always based ultimately upon the spatial locality of interatomic interactions. At some point, moving a sufficiently remote atom at \mathbf{R}' will make no significant difference on at atom at \mathbf{R} if $|\mathbf{R} - \mathbf{R}'|$ is sufficiently large [33]. As the electronic structure determines the interatomic interactions, it must also determine this range. The quantity providing this information turns out to be the decay of the single-particle density matrix. Depending on the accuracy needed, the range of the density matrix is at least several Å in semiconductors and farther in metals [34, 35]. A real-space localized representation can be exploited for this purpose too, the "maximally localized" Wannier functions [36], variants of which may be computed efficiently by projection into the occupied electronic subspace [37, 38].

1.7 What DFT can Provide

Standard DFT codes produce a cornucopia of data: total energies, forces, structure, dynamics (these can usually be quite well represented) and atomic charges. The electronic structure is a trickier undertaking if one considers excited states, since DFT is a *ground state* method. To even estimate a hypothetical optical gap, additional methods beyond DFT are required. Of course excited states are required for optical and transport calculations. The band gap problem has been practically addressed by computations with "hybrid functionals", especially the popular Heyd, Scuseria, Enzerhof [39] ("HSE06") approximation. For correlated electrons, computationally demanding methods are possible such as the GW approximation, "dynamical mean field theory" and other topics treated by Martin, Reining and Ceperley [40].

1.8 The Emerging Solution for Large Systems and Long Times: Machine Learning

While my palantir is probably murkier than most, I can make one prediction: Machine-Learning (ML) methods will transform this field. The revolution is already underway. Of all the myriad potential uses of ML we are thinking of a specific one: ML based interatomic potentials. There have been several attempts here. We mention the one that we know the most about, the GAP potential [41], owing to our good fortune to collaborate with the pioneers of the method, and direct the reader to the burgeoning literature on the subject.

A naïve but helpful way to think about ML approaches to interatomic potentials is to interpret it as a sophisticated interpolation scheme. An ML potential is of course only as good as the information that is 'fed' to it. The information takes the form of a large number of atomic configurations, and for each of these the total energy and forces on the atoms computed from an accurate (probably DFT) code. The idea is that if enough of these configurations is available, then one could undertake a new simulation only using information in the database – if "new" configurations were close enough to existing conformations in the database to enable sufficiently accurate "interpolation". Of course, the devil is in the details: what does the metric on configuration space "close enough" mean and how does one really "interpolate". After a lot of very ingenious work [42], there are quantitative answers to these questions and furthermore what is not *a priori* obvious is that the method is quite practical.

1.9 Modeling with Experimental Information: Let the Data Speak for Itself

The most important test that computer generated models of materials have to pass is agreement with the experimental findings. Accuracy of these models are often measured in terms of how close the model aligns with the experiments. The routine melt quench (MQ) technique suffers from fast cooling rate and does not always produce experimental signatures. Efforts have been made to create models by using experimental information as input to drive the atoms. The first efforts in this direction was made by McGreevy and Pusztai who introduced Reverse Monte Carlo (RMC) simulations for amorphous materials [43]. This idea was later extended by M. G. Tucker and coworkers [44] by developing RMCProfile. Conventional Reverse Monte Carlo approach produces incorrect chemical ordering or an overly disordered configuration unless one includes additional constraints to compel specified local order. However, incorporating multiple constraints in cost function makes inversion problem more challenging while adding bias to the resulting model. To overcome this hurdle and make effective use of experimental information available, a hybrid method called Experimentally Constrained Molecular Relaxation (ECMR) was developed by Biswas and coworkers [45]. ECMR suffered with the configurations being trapped in local minima and required a new start. To get around this problem, Pandey and coworkers developed Force Enhanced Atomic Refinement (FEAR) [46] using incremental minimization. The idea behind FEAR is to solve the minimization problem:

$$\phi = E\left(\vec{R}\right) + \chi^2 \Lambda \tag{1.1}$$

where E is the total energy, $\Lambda(> 0)$ determines the relative weighting of the experiment and the potential. χ^2 provides a measure of the experimental fitting,

$$\chi^{2} = \sum_{i=1}^{N} \frac{\left(F_{i}^{calc}(\vec{R}) - F_{i}^{exp}\right)^{2}}{\sigma^{2}}$$
(1.2)

where \vec{R} is the set of coordinates of all the atoms, N is the number of data points in the experimental data set, and σ takes into account the experimental uncertainty. For example, if one is using neutron structure factor as experimental input, F_i^{calc} and F_i^{exp} are the S(Q) values at each *i* (or each *Q*) for the models and the experiment, respectively. Similarly, one could also use the real space experimental information as input. Since the simultaneous minimization of both the quantities on the right hand side of Eqn. 1.1 is extremely difficult, we solve this problem by separate incremental minimization of each quantity. Details of FEAR simulation technique can be found elsewhere [46–48].

1.10 Characterizing Amorphous Materials

1.10.1 Structural Features

A principal goal of structural analysis of amorphous materials is to correlate the atomic structure with the observed properties and understand the properties at an atomistic level. The ideas gained from these analyses helps researchers optimize the material with the desired properties. In amorphous materials, the properties are not determined by the absolute position of atoms, but by the relative position of atoms close together and interacting with each other [49]. The arrangement of atoms in real space and thus the bonding environment is studied using the radial distribution function (RDF) defined as:

$$g(r) = \frac{N}{4\pi r^2 V} \frac{dn(r)}{dr}$$
(1.3)

where N and V denote the total number of atoms and the volume of the simulation box respectively. dn(r) denotes the number of atoms located at distances lying between r and r+dr. The radial distribution function g(r) gives the probability of finding an atom in a shell of thickness dr at a distance r from a reference atom. For multi-species systems, the partial radial distribution function is defined as:

$$g_{\alpha\beta}(r) = \frac{Nc_{\alpha}}{4\pi r^2 V} \frac{dn_{\alpha\beta}(r)}{dr}$$
(1.4)

where c_{α} is the concentration of α atomic species. The functions $g_{\alpha\beta}(r)$ enable the computation of the probability of finding an atom of type β at a distance *r* from the reference α atom.

The RDF is a popular structural analysis tool also because it facilitates direct comparison with experiment as RDF can be obtained from experiments by performing a Fourier transform of the static structure factor S(Q) [50],

$$g(r) = 1 + \frac{1}{2\pi\rho_0} \int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ$$
(1.5)

The first peak, together with the first minimum, in RDF describes the short range order present in the system. The medium range order indicates the position and shape of the intermediate peaks beyond the first peak minimum up to several Angstroms. Due the the inherent lack of long range order, RDF saturates to unity for long distances. The peaks in the RDF for amorphous materials become broader with increasing distance from the reference atom unlike crystals. As a consequence of this broadening in the RDF peaks, the structure of the non-crystalline solids cannot be determined uniquely from experiment.

The RDF presented in this dissertation have been calculated using an open source program ISAACS [51]. A detailed discussion of the various structural analysis functions can be found in [44, 50, 52]. There are different definitions and terminology for the total scattering functions and their real-space counterparts. A detailed description of various functions and comparison between definitions used by various group of researchers can be found in the popular article by David Keen [52].

1.10.2 Electronic Properties

The electronic structure of amorphous materials is studied using the total electronic density of states (EDoS), partial DoS, and inverse participation ratio (IPR). These quantities help us in several ways: to validate/invalidate the models, understand the conducting/insulating behavior, and study the extent of localization of electronic states. In this dissertation, single particle Kohn-Sham eigenvectors derived using density functional theory based calculations are taken as electronic states. The EDoS thus represents the density of Kohn-Sham states plotted against the energy. For finite systems, the EDoS is a discrete quantity defined as:

$$D(E) = \frac{1}{N} \sum_{i}^{N} \delta(E - E_i)$$
(1.6)

where N represents the size of the basis set and E_i is the eigenvalue of the ith eigenvector. The conduction in amorphous systems depends mainly on the density of states and the

3.7

extent of localization of the Kohn-Sham states near the Fermi level. An account of the localization of Kohn-Sham states is given by IPR defined as:

$$I(\psi_n) = \frac{\sum_i |a_n^i|^4}{\left(\sum_i |a_n^i|^2\right)^2}$$
(1.7)

where a_n^i is the contribution to the eigenvector ψ_n from the *i*th atomic orbital (s, p, and d) as calculated with VASP. Putting the definition in simpler terms, localized states have high IPR value (ideally equal to I = 1) while an ideally extended state having a value of (1/N), i.e. evenly distributed over N atoms.

1.10.3 Vibrational Properties

The analysis of the vibrational properties of amorphous materials not only provides a useful insight to the local bonding environment but also helps understand the thermal and mechanical properties. Vibrational properties of the models were studied using the harmonic approximation. The Hessian matrix is computed by displacing each atom in 6-directions ($\pm x$, $\pm y$, $\pm z$) by 0.015 Å. The few lowest frequencies arising from rigid supercell transitions were removed from the calculations of the vibrational density of states (VDoS). The VDoS is defined as:

$$g(\omega) = \frac{1}{3N} \sum_{i=1}^{3N} \delta(\omega - \omega_i)$$
(1.8)

with *N* and ω_i representing the number of atoms and the eigenfrequencies of normal modes, respectively. This definition suggests that any frequency that has larger number of eigenfrequencies in its neighborhood will have a higher VDoS.

Vibrational excitation in crystals are extended and show plane-wave-like behavior. The translational periodicity leads to the observed departure from the Debye models at short wavelengths. For wavevectors comparable to the zone boundary value (π /a), the phonon dispersion curves flatten, leading to van Hove singularities in the VDoS [53].

Vibrational excitation in amorphous materials differ greatly from the extended plane-wave like phonons in crystalline materials. The absence of translational symmetry smooths out the van Hove singularities [53], as also seen for electrons.

The extent of localization of each normal mode frequency is studied using the vibrational inverse participation ratio (VIPR) defined as:

$$\mathcal{V}(\omega_n) = \frac{\sum_{i=1}^{N} |\mathbf{u}_n^i|^4}{\left(\sum_{i=1}^{N} |\mathbf{u}_n^i|^2\right)^2}$$
(1.9)

where \mathbf{u}_n^i is displacement vector of i^{th} atom at normal mode frequency ω_n . By definition, low values of VIPR indicate vibrational mode evenly distributed among the atoms while higher values imply only a few atoms contributing at that particular eigenfrequency.

1.11 Dissertation Outline

The rest of this dissertation is organized as follows: In chapter 2, we present the simulation of graphitization using *ab initio* and machine learning techniques. We discuss the structure and electronics of the amorphous graphite models and compare them with crystalline graphite whenever possible. In chapter 3, we present our findings on the research involving amorphous carbon and carbon foam. The FEAR modeling of annealing induced changes in amorphous ZrO_2 -Ta₂O₅ is discussed in chapter 4. Results from the study of GeSe glasses using FEAR is discussed in chapter 5. In chapter 6, we discuss the growth of conducting Cu filament in an insulating Ta₂O₅ host. In chapter 7, we discuss the conclusions and future directions.

2 SIMULATION OF GRAPHITIZATION USING AB-INITIO AND Machine Learning Techniques

The work related to amorphous graphite presented in this chapter has been published as **R. Thapa, C. Ugwumadu, K. Nepal, J. Trembly, and D. A. Drabold**, *Ab Initio* Simulation of Amorphous Graphite, Phys. Rev. Lett. **128**, 236402 (2022) [54].

2.1 Introduction

Owing to a wide variety of bonding environments, different carbon materials exist. For example, diamond has all its C atoms fourfold coordinated while graphite has threefold. Graphene, a material of massive research and economic interest, is a plane of C atoms all connected to three C atoms at fixed bond length and bond angles. Carbon-based materials seem to have unlimited potential applications and interest [55–57], from life to Bucky Balls, and they continue to yield scientific surprises and new applications. Graphite is an important, commonly available carbon material with many uses. A burgeoning application for graphite is for battery electrodes in Li ion batteries [58] and is crucial for the electric vehicle industry—a Tesla model S on average needs 54 kg of graphite [59]. Such electrodes are best if made with pure carbon materials, which are becoming more difficult to obtain owing to spiraling technological demand. It is therefore of interest to determine novel paths to synthetic forms of graphite from naturally occurring carbonaceous material such as coal. This raises several questions: (1) Is it possible to convert such materials into a graphitic phase? (2) What impurities will remain and with what technological consequences? (3) What are the resulting properties (structural, mechanical, electrical and thermal) of such materials?

We have discussed an amorphous phase of monolayer graphene, based on structural models involving pure sp² bonding with ring disorder (that is, rather than a 2D net

consisting only of hexagons, we allow for pentagons, heptagons, etc.). Among other findings, we noted that the presence of pentagons in such a structure induces puckering (departure from ideal planarity) from the strain of the ring defect using *ab initio* methods [60, 61]. The semimetallic character of perfect graphene is transformed by ring disorder [62, 63]. Recently, experimental synthesis of monolayer amorphous graphene using chemical vapor deposition has been reported [64]. On the theoretical side, two dimensional amorphous graphene structures created by quenching the high temperature liquid state using Tersoff-II [65] potential has been reported [66]. Graphitization of amorphous carbon under electron irradiation has been studied experimentally and theoretically [67].

In this chapter, we employ an *ab initio* method to unveil a layering transition from either amorphous carbon or even *random* starting models into a structure consisting of planes of monolayer amorphous graphene separated by ~ 0.3 nm, the interlayer separation in graphite, as a consequence of annealing such models with first principles interactions at a temperature of about 3000 K, and for a density range of ca. 2.2–2.8 g/cm³. These sheets are sp², but with ring disorder (pentagons, hexagons, heptagons). We name this material "amorphous graphite" (a-G). We elucidate the transition in atomistic detail. The a-G structure cannot exactly reproduce AB stacking, yet even with ring disorder on the planes, has a total energy only 0.32 eV/atom above crystalline graphite (c-G). We examine the electronic origins of cohesion by analyzing electronic structure in the galleries, and demonstrate how ring disorder reduces in-plane electron transport. This work takes a step toward realizing the goal of synthetic graphite, and may offer clues to layering processes in other systems such as metal dichalcogenides. It has been suspected from experiments that graphitization occurs near 3000 K [68–72], but the details of the formation process and nature of disorder in the planes were unknown. From a modeling viewpoint, *ab initio* simulations of complete or partial ordering are rare and important, the best example being phase-change memory materials [73, 74].

2.2 Computational Details

Our simulation involved constant volume simulations carried out with either (1) *ab initio* models of a-C simulated for the selected density [75] or (2) *random* starting configuration for the desired density. These configurations were annealed to T = 3000 K using a Nosé-Hoover thermostat [76, 77]. Provided the density was within the 2.2–2.8 g/cm³ range a layering transition was always observed. The final structure after the annealing was topologically unchanged by a CG relaxation, and the structure maintained the layered structure in subsequent MD simulation. Total simulation time ranged from 100 to 500 ps. We carried out the simulations with VASP [78] using projector augmented wave [79] potentials and the Perdew-Burke-Ernzerhof (PBE) [80] exchange-correlation functional. For the purpose of completeness and comparison, we also used the DFT-D3 Van der Waals (vdW) corrected functional [81], and the accurate local-density-approximation-trained machine learning (ML) Gaussian Approximation Potential (GAP) of Deringer and coworkers [5, 6].

The results obtained with different approaches were essentially identical: consistent a-G formation in the density and temperature window. Low density a-C (< 2.0 g/cm³) had a significant sp³ to sp² conversion but weak layering (undulating wormlike layers), while high density a-C (> 3.0 g/cm³) did not layer. No layering was seen under simulation at temperatures higher than 4000 K. The linear scaling GAP potential enabled much larger simulations than VASP. In contrast, identical simulations with REAX-FF [82] or Tersoff [83] potentials showed no layering. In Table 2.1, we summarize the simulations details for the models generated for this work. τ is the simulation time required for layering to become clear, and is reasonably consistent over all the simulations, methods,

Model	Size	au (in ps)	$\delta E_{\rm atom}({\rm in \ eV})$	Functional	Initial State
M1	160	45	0.00	PBE	amorphous
M2	160	95	0.10	PBE	amorphous
M3	160	130	-0.04	PBE+vdW	amorphous
M4	80	40	0.13	PBE	random
M5	400	50	0.08	GAP-ML	random
M6	1000	60	-0.04	GAP-ML	random

Table 2.1: Simulation parameters for various models of a-G obtained by NVT simulation at 2700 K. Difference in energy per atom, computed with PBE, is compared to M1.

and over the system size. Finite-size effects were investigated by generating models ranging from 80–1000 atoms, and the GAP potential revealed an identical layering with comparable τ . This and the consistent form of the a-G implies that our observations are not very sensitive to size effects. We infer that the layering transition temperature is near 2700 K, provided the simulation is run for a considerable time (~ 100 ps) with accurate interatomic interactions. A transition temperature of 3000 K has been observed experimentally for production of high quality graphene using flash graphene synthesis [84].

2.3 Results

The structural transition of the a-C network from disordered phase under NVT simulation at different temperatures is shown in Fig. 2.1 (top) for models M1 and M2. Atoms in the figures are color coded: yellow for sp², red for sp³ and green for sp. This color nomenclature will be used throughout this chapter unless otherwise stated. Since c-G is completely sp² with flat layers, we consider our models to be graphitized into a-G if

they have a significant fraction of sp^2 bonding (> 95%) and are layered. Following this definition, we see from Fig. 2.1 (top) that graphitization only happens at and above 2700 K in both models with an interplanar separation in the range 3.05 ± 0.06 Å. However, there is a significant increase in the fraction of sp² atoms even at 2500 K. This temperature-induced transition from sp^3 to sp^2 bonding in nanodiamond and adamantane has been studied experimentally using Raman spectroscopy [68]. Zero pressure relaxation of the a-G models M1 and M2 with vdW interactions produced a lower energy configuration accompanied by an increase in volume. This volume rise lowers the density to 2.15 g/cm³ and increases the interlayer separation to 3.30 ± 0.05 Å, notably close to graphite. In contrast to c-G with regular ordering between adjacent layers (AA, AB stacking), there is no such stacking of the layers in a-G, a consequence of the presence of topological (ring) disorder in the planes. In Fig. 2.1 (bottom), we show the in-plane radial distribution functions for the models. The first peak is centered around the graphitic bond length and the width of the peaks arises from disorder-induced deviations in bond length from the ideal graphite bond length. The largest model M6 with 1000 atoms produces extended ordering beyond the first neighbor with clear peaks at 2.45 Å and 2.85 Å.



Figure 2.1: (**Top**): Conjugate gradient relaxed structure of M1 (top) and M2 (bottom) after NVT simulation at 300 K, 2500 K , 2700 K, 3000 K, 3300 K.

(**Bottom**): In-plane radial distribution function of the representative models. The dashed line indicates the graphite bond length. The inset shows the arrangement of atoms in a representative layer in an a-G.
To study the origin of layering, we tracked where the atoms forming the layers were located in the originally disordered structure; see Fig. 2.2 (top). The atoms in a particular layer of a-G are members of a connected network in the a-C. The disorder-to-order transition seems describable with a nucleation theory picture with seeds of sp² carbon growing into larger planar structures, enabling layering.

Figure 2.2 (bottom) treats the time evolution of the transition in detail for M2; similar results were obtained for the other models. The planarity fraction is computed using the odds ratio for the likelihood of atoms forming planes. The peculiar peaks around 6 ps and 57 ps suggest sharp rearrangement of atomic positions to achieve planar configurations with a higher fraction of sp² bonding. These configurations underwent additional substantial rearrangements before yielding a-G. It is worth mentioning that after 95 ps the layering order parameter exhibited reduced fluctuations as the system stabilized at an optimized energy, as seen in the flat tail for the total energy curve (in blue).



Figure 2.2: (**Top**): Positions of atoms forming different layers in a-G for M2 at 2700 K. Atoms forming different layers are shown in different colors.

(**Bottom**): Layer formation and total energy (plotted as a moving average over 2 ps) as a function of simulation time. The insets show the snapshots of the atomic configurations at different points in time.

The charge-density distribution for the M2 model simulated at 2700 K has been presented, together with similar calculations for c-G for comparison, in Fig. 2.3. The charge distribution was calculated using the Heyd, Scuseria and Ernzerhof (HSE06) hybrid functional [39, 85, 86] and has been plotted along two neighboring planes of atoms [labelled (a), (e)] and three other parallel, equally spaced slices [labelled (b), (c), (d)] in between them (in the gallery). For comparison, respective planes in a-G and c-G have been plotted within the same color range. For plane (c), the color map shows contributions from both planes. The color maps for a-G show a more disordered distribution of charges along the planes of atoms, compared to the c-G, particularly because of the presence of bond-length or bond-angle distortion, ring disorder induced puckering, etc. Our calculations have also indicated that the variation of the charge density values for the a-G is higher than graphite because of the disorder. The charge distribution in the a-G galleries exhibits a low-density delocalized electron gas with higher charge on the plane of atoms and monotonically decreasing as we move away into the gallery. However, we should note that the majority of the charge density on the most isolated layer from the plane of atoms, plane (c) in Fig. 2.3, is greater than 2% of the maximum charge density on the plane of atoms [layer (a) and (e)] suggesting the presence of a fairly homogeneous electron gas in the galleries built from the bonding orbitals formed from the π electrons. The electronic density of states (DOS) of a-G revealed a broad peak at the Fermi level and had no semi metallic DOS characteristic of c-G.



Figure 2.3: (**Top**): Charge density distribution on two neighboring graphitized planes for M2 model simulated at 2700 K and three equally spaced slices between them.

(**Bottom**): Similar illustration for c-G (lower panel) is included for the purpose of comparison. Black circles in (a) and (e) mark the position of the atoms in the plane.

In Fig. 2.4, we present information on the band-decomposed charge densities for the a-G. Bands close to the Fermi level (E_f) contain the π ($E < E_f$) and π^* ($E > E_f$) electrons. The π bands involve much mixing from π orbitals on different sites. Figure 2.4(a) shows the π mixing for 3 π bonding orbitals, the π electrons from these bands extend into the gallery, creating binding between layers separated by roughly 3.1 Å. Figure 2.4(b) shows the π^* antibonding orbitals with no charge projection to the gallery. The evidence of the electron delocalization is further illustrated by projecting the charge density from the 3D box into a plane for a single π band and a symmetric π^* band in Figs. 2.4(c) and (d), supporting the presence and absence of the charge density in the gallery for the π and π^* orbitals respectively. The presence of such delocalized π electrons in the galleries has been suggested for graphite, where it was argued that the graphene bonding forces are dominantly metallic and not Van der Waals [87, 88]. Our work suggests that while Van der Waals plays a role in layering and binding, other contributions within local density approximation or PBE also play an important role.



Figure 2.4: Details of band-decomposed charge densities for the a-G for (a) 3 π bands (colored blue, green, and red) in the valence region and (b) their correspondingly symmetric π^* bands in the conduction region. We also show the charge distribution for a pair of nearly symmetric bands in (c) the valence region and (d) the conduction region.

To study the effects of disorder on the electronic conduction and visualize the conduction-active regions in the network, we calculate the space-projected conductivity (SPC) [89] on a-G and compare it with that of c-G. The SPC exploits the Kubo-Greenwood formula to obtain information about conduction pathways in materials. The SPC projected onto particular layers of atoms is shown in Fig.2.5. The SPC of an ideal graphite layer with no defects has clear paths for conduction in the plane. However, in graphite with a 5-8-5 ring defect, the conduction in the regions connecting the pentagons with the octagon is significantly reduced but the conductivity is still high in the regions dominated largely by hexagons. This reduction in electric conductivity in a 5-8-5 defected graphene has been previously reported [90]. Similar findings were seen for our atomic layers in a-G whereby the conduction paths try to avoid a junction involving a ring disorder. In other words, conduction is favored along connected atoms in hexagonal rings over non-hexagon rings. The presence of topological ring disorder significantly affects the

charge transport in both graphite and a-G. We also found that the conductivity value in pure graphite is highest, followed by 5-8-5 defect graphite. The a-G conductivity was decreased by a factor of about 10^{-2} relative to graphite.



Figure 2.5: SPC results (gray isosurface) for (a) an ideal graphene layer, (b) a graphene layer with 2 vacancies, (c) M1, and (d) M2. Atoms in pink in (c) and (d) show atoms forming conduction paths in the spatial grid, while atoms in black are border atoms where one or both neighboring rings are non-hexagon rings. Green colored atoms in (d) are consistent for sp atoms in M2.

2.4 Conclusions

We present evidence that a-G exists and we describe its process of formation in detail. Since the plane formation is found to be robust in a suitable temperature or density window, a-G growth may be a practical means to obtain amorphous graphene planes in a layered graphite-like superstructure, that might even be exfoliated. The in-plane electronic conductivity is expected to be much lower compared to graphite and consider this to be another signature of a-G. We analyze the electronic structure, the mechanism of cohesion and the electronic consequences of topological (ring) disorder using the space-projected conductivity.

3 ATOMIC SCALE STUDY OF CARBON FOAM

3.1 Amorphous Carbon

Carbon foams are made up of a dense carbon matrix comprising of amorphous Carbon (a-C) together with large macroscopic pores distributed in space. Therefore, to get started, it is pivotal to understand the structure, mechanical, thermal, vibrational, and electronic properties of a-C to better understand and optimize the properties of carbon foams.

To understand the density dependence of the structure, bonding environment, and mechanical properties of amorphous Carbon (a-C) we have studied models of a-C at various densities $(0.75 \text{ g/cm}^3 - 3.5 \text{ g/cm}^3)$ using plane-wave basis set density functional code Vienna *ab initio* Simulation Package (VASP) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional under generalized gradient approximation (GGA). The pseudopotential used throughout the calculation was constructed under the projected augmented wave (PAW) method. Since the properties of any a-C material is significantly affected by the fraction of different hybridization (or coordination), we present these quantities in Fig. 3.1 (left panel). The figure shows an increasing fraction of sp³ C atoms accompanied by a decrease in the sp fraction with increasing density. The sp² fraction increases reaches a plateau near the graphite density and then decreases with increasing density. The dependence of the mechanical properties on the density of a-C is shown in Fig. 3.1 (right panel). The figure suggests that the mechanical strength of a-C rises monotonically with density.



Figure 3.1: Bulk and Shear modulus (right panel) of a-C at various densities plotted with the fraction of different hybridization (left panel) present in them.

Heat treatment of the carbon foams, extruded at ISEE, performed at various temperatures ranging from 1000 K – 1400 K revealed interesting variations: the measured C, H, N, S, O compositions and the electrical conductivity was very dependent on the annealing temperature. To simulate this thermal annealing induced change in the foams, we carried out simulations at different temperatures (up to 1500 K) on a model of a-C at 2.0 g/cm³ using VASP.



Figure 3.2: Fraction of different hybridization as a function of annealing temperature.

In Fig. 3.2, we plotted the fraction of various bonding environments around C atoms as a function of annealing at different temperatures. The rise in sp bonded C-atoms could explain the observed difference between the as-extruded foam and the heat-treated foams. The space projected conductivity (SPC), that projects the electrical conductivity on to real space, has shown sp atoms to be highly conductive compared to other hybridization [89]. This suggests an increasing electrical conductivity with annealing temperatures up to 1500 K which is in close agreement with observed conductivity measurements.

3.2 Surface Reactivity of Amorphous Carbon

A slab was created out of the amorphous models (2.0 g/cm³ and 3.5 g/cm³) by breaking the periodic boundary condition along the z-axis. We chose to work with a 2.0 g/cm³ model in accordance with the density from carbon foam created using bituminous coal [91]. The removal of periodic boundary conditions robs neighbors from the atoms close to the surface. To simulate the surface reconstruction in these models, the slabs were then taken through a NVT simulation at 300 K for 6 ps using plane-wave DFT code VASP as above. After the NVT run, the slab was taken through a conjugate gradient relaxation until the magnitude of the force on each atom was reduced to less than 0.02 eV/Å. During the NVT cycle and subsequent CG minimization, the under coordinated atoms on the cleaved surface that formed dangling bonds sticking out from the surface were passivated by bonding them with nearby C atoms.



Figure 3.3: Mechanism of O_2 interaction on the surface of a-C. The O_2 molecules stick to active C sites on the surface (b), break the O-O bond (c), and then come off as CO molecule (d).

To study the reactivity of the surface, we perform NVT simulation of the surface model with O_2/N_2 adsorbate at different temperatures (300 K, 1000 K, 2000 K). Our calculations show that the surface of a-C is resistant to reaction by O_2/N_2 at room temperature. However, at higher temperatures (1000 K, 2000 K), sp hybridized atoms on the surface get ripped off by O_2 and are ejected as CO/CO_2 . A schematic diagram of the O_2 molecule reaction on the a-C surface at 1000 K is shown in Fig. 3.3.

The figure shows that O_2 molecules stick to active sites (usually an sp) on the surface before dissociation and then sticks onto a C atom. The adsorbed compound desorbs out to the atmosphere as CO gas. This finding provides an explanation for the weight loss of carbon foams under heat treatment in O_2 atmosphere seen in TGA experiments. Also, sp C atoms at different environments (long, bent - atoms with C-C-C bond angles less than 150° are considered bent) have varying levels of susceptibility of getting ripped off: only long sp C atoms get ripped off at 1000 K while at 2000 K both long and bent sp get ripped off.

On the other hand, we find that an a-C surface does not adsorb the N_2 molecules even at higher temperatures. The N_2 molecule neither breaks nor sticks to an active C site on the surface as the O_2 molecule does thereby explaining almost zero weight loss under heat treatment in nitrogen environment.

To study how favorable adsorption is on the a-C surface; we calculate the adsorption energies for the O_2 and N_2 molecules at C atoms on the surface with different bonding environment. The adsorption energy (E_{ads}) of a particular adsorption process is defined as follows:

$$E_{ads} = E_{total} - (E_{slab} + E_{adsorbate})$$
(3.1)

where E_{total} represents the total energy of the slab with the adsorbate. By definition, negative adsorption energy implies energetically favorable adsorption. The calculated adsorption energies are presented in Table 3.1.

Site	Adsorbent	E_{ads} (eV)
long sp	O ₂	-3.41
bent sp	O ₂	-6.28
sp ²	O_2	-2.29

Table 3.1: Adsorption energies of the O₂ molecules on different sites of the a-C surfaces.

Our calculations show that O_2 adsorption is energetically favorable while N_2 adsorption is not. Furthermore, adsorption of O_2 on a bent sp C atom is energetically more favorable than on long sp, in line with previous ML based calculation [92]. This explains

why bent sp carbon atoms do not get excised off by O_2 at 1000 K but only do so at 2000 K where the kinetic energy is strong enough to overcome this adsorption energy.

Additional simulations were carried out to study the behavior of water molecules near the surface. Water molecules are attracted by sp atoms, with the attraction being strong on a bent sp atom compared to the long sp atoms, in a way like the O_2 molecules.

3.3 Carbon Foam Modeling

Carbon foams, a new age functional material with cellular structure, demonstrate numerous unique properties thereby making it an attractive material for insulating [93], electromagnetic interference (EMI) shielding [94, 95], and energy-absorbing applications [96]. The inherent porosity and light-weight also make them attractive material for light-weight applications in advanced aircraft and spacecraft structures [97]. These plethora of applications of a relatively cheap material has led to the growth of industries, like CFOAM in Triadelphia, WV, dedicated to production on an industrial scale.

Efforts have been made to characterize and optimize carbon foams using various experimental techniques [98] and modeling schemes [99–101]. One popular modeling scheme for carbon foams is the finite element analysis (FEA) method which involves modeling the properties of interest on finite sized computer-assisted-design (CAD) models [102, 103]. The understanding of carbon foam properties also requires a clear understanding of a-C structure because the dense matrix within the carbon foam are made mostly of a-C. Several atomistic models of a-C are now available in literature [5, 6, 54, 75, 104, 105]. The findings from atomistic studies of amorphous carbon materials coupled with other FEA modeling studies leads us towards a better understanding of the carbon foams.

In order to understand the atomistic details of carbon foams, we need to create reliable atomic models that topologically resemble actual carbon foams. Since the actual length scale on a C-foam is of the order of hundreds of micrometers, creating atomic models in this length scale in impossible. To simulate the C-foam, we use an algorithm to create C-foam like structures but in nanometer length scale. This modeling scheme bridges the GAP between the finite element modeling and the atomistic simulation of a-C (presented in Chapter 3.1). We create structures that resemble real carbon foam in appearance but in a nanometer length scale. In order to create the models of the C-foam, we follow the following procedure:

- estimate the density, number of atoms, and box size
- determine the porosity, number of pores and pore radius

$$Porosity = N_{pores} \times V_{pore} \tag{3.2}$$

where V_{pore} , a dimensionless quantity, is the relative volume of pore with respect to the volume of the box.

- place the pore centers appropriately far enough to produce the desired porosity
- place atoms randomly but not falling inside the pore volume. The atoms are placed with periodic boundary condition intact.
- anneal the models near 1000 K with reliable interatomic potential in order to remove artifacts from random placements of atoms
- to get to a better energy minimum, take the final model from the NVT cycle through a energy minimization routine

We created foam models with 8000, 11000, 12000 atoms while keeping the box size and porosity constant. All the foam models were built using machine-learned GAP

Density (g/cm ³)	r _{pore}	n _{pore}	sp	sp ²	sp ³
0.50	0.28	6	42.10	54.40	1.20
0.70	0.30	6	23.90	71.50	4.10
0.75	0.30	6	21.50	72.40	5.50
0.75	0.27	8	25.10	68.40	5.60

Table 3.2: Pore radius r_{pore} (in units of box length) and distribution of different bonding environments around the C-atoms among different foam models.

(Gaussian Approximation Potential) potential in LAMMPS [106] to allow the system to reduce stress and get rid of nonphysical bonds. The details from these foam models are presented in Table 3.2. It shows that higher coordination increases with density. Also, for the same density, a higher number of pores (smaller pores) implies larger fraction of sp atoms. A structural model of a foam model generated using this procedure has been shown in Fig. 3.4 (top). The figure shows connected networks of C matrix with large pores between them. Despite being far smaller than the real foams, the models bears an uncanny resemblance to the CT scans of real carbon foams. The internal structure and the bonding environment in the dense regions of the foam models are shown in Fig. 3.4 (bottom). The internal structure reveals a presence of twofold, threefold, and fourfold coordinated carbon atoms. Unstable carbon configurations like the dangling bonds are absent in the carbon matrix and the arrangement of atoms is disordered. This could serve as a model of the dense carbon matrix in real carbon foams.



Figure 3.4: (**Top**): Structure of 8000 atom foam model created using ML GAP potential. (**Bottom**) Internal Structure of the carbon matrix in the foam models. Red, yellow, green, and blue atoms represent fourfold, threefold, twofold, and onefold coordinated C atoms.

3.4 Conclusions

The structure of a-C was studied over a wide range of densities. Surface reactivity and the mechanism of reaction of atmospheric gases on the surface of a-C were studied. Annealing of a-C at temperatures below 1500 K revealed an observable increase in the fraction of sp atoms. This rise in sp atoms enhances the electrical conduction because space projected conductivity calculations have shown that sp atoms offer less resistive path to electronic conduction [89]. Foam models were created using ML-based GAP potential and discussed in detail. This could lead to ways to understand the dependence of mechanical properties of the foam on the density, porosity, pore size, etc on models that are much larger compared to the *ab initio* models created with VASP. The presence of huge pores on these foam models would provide a better picture of the surface reactivity of these real carbon foam models to external adsorbents (N₂, O₂, H₂O).

4 ANNEALING INDUCED CHANGES IN MIRROR COATINGS

The work related to zirconia doped tantala presented in this chapter has been published as **R. Thapa, K. Prasai, R. Bassiri, M. M. Fejer, and D. A. Drabold**, Realistic computer models of amorphous ZrO₂:Ta₂O₅: Structural, optical, and vibrational properties, Phys. Rev. B **105**, 224207 (2022) [7].

4.1 Introduction

Brownian thermal noise associated with the dielectric coatings limits the sensitivity of interferometric gravitational wave detectors such as LIGO and Virgo [107–109]. These coatings consist of alternating layers of high and low refractive index materials. In the current generation of LIGO and Virgo, silica (SiO₂) and titania-doped tantala (TiO₂:Ta₂O₅) are used as the low and high index material, respectively [109]. The measured mechanical loss angle for the state-of-the-art ion-beam-sputtered SiO₂ coatings is 4×10^{-5} rad [110, 111] while that for TiO₂:Ta₂O₅ is 2.4×10^{-4} rad [112, 113]. Hence, the dominant contributor to the coating thermal noise is high index TiO₂:Ta₂O₅ layer. One of the ways of reducing coating thermal noise and increasing the sensitivity of future upgrades of these detectors is to find a low-mechanical-loss replacement for the high-index layer.

Zirconia-alloyed tantala ($ZrO_2:Ta_2O_5$) has been studied as a promising candidate to replace the high index layer [107, 109]. In addition to having higher refractive index (> 2 at 1064 nm) compared to silica (1.45 at 1064 nm), $ZrO_2:Ta_2O_5$ appears to remain amorphous after annealing up to the temperatures of 800°C while most other Ta_2O_5 -based coatings could be annealed without crystallization only up to 600°C. This is significant because post-deposition annealing is a standard procedure to reduce room-temperature (RT) mechanical loss of amorphous oxide coatings. Measurements have shown this to be true for $ZrO_2:Ta_2O_5$ as well – measured values of RT loss are seen to decrease monotonically as these coatings are subjected to higher and higher annealing temperatures before the crystallization starts [107]. Since annealing the low index layer SiO_2 also drives down its mechanical loss, this recipe could form a potential route to low thermal noise high-reflection (HR) coating.

In order to understand the origin of mechanical loss in the thin films of ZrO_2 :Ta₂O₅ and possibly find ways to reduce the loss, it is important to study its atomic structure and the ways two-level systems (TLSs), which are thought to be responsible for loss processes, could form in its structure. Furthermore, since the RT mechanical loss values of ZrO_2 :Ta₂O₅ continuously decrease upon annealing [107], it could be especially informative to probe the annealing-induced effects on its atomic structure and how those changes in atomic structure might relate to an observed decrease in RT mechanical loss.

In an earlier work published by the Prasai *et al.* [109], x-ray grazing incidence pair distribution function (GIPDF) measurements carried out on differently annealed thin films of ZrO_2 :Ta₂O₅ are reported. These measurements are then employed to generate structural models of ZrO_2 :Ta₂O₅. Generating several sets of models based on GIPDFs measured on differently annealed samples allowed the study of annealing-induced effects on atomic structure. The modeling method employed in this work is force-enhanced atomic refinement (FEAR) [46, 47]. FEAR uses force-based energy minimization to constrain the solution space of reverse Monte Carlo (RMC) modeling so that the resulting models are simultaneously in agreement with scattering data as well as are low energy configurations respecting the chemical and topological order required by the chosen force field.

In this chapter, we revisit the atomic modeling part of Ref [109] employing density functional theory (DFT)-based calculations for energy minimization instead of two-body empirical force field used in Ref [109]. We gain significant accuracy in modeled atomic interactions by using DFT-based calculations compared to the simple 2-body empirical forcefields. Furthermore, electronic and optical properties of the models could be calculated using the DFT based calculations. However, the size and number of instances we could model the system are significantly limited in the present work compared to Ref [109] and hence our ability to resolve small differences between differently annealed systems is poorer in the present work compared to Ref [109]. Based on the new models we generate, we report on several characteristics – including coordinations, polyhedral connections, bond angle distribution, voids, electronic and phonon density of states and refractive index. The optical properties are of special interest to LIGO and VIRGO applications.

4.2 Methodology and Models

We prepare 416-atom FEAR [46, 47] models at experimental density (6.53 g/cm^{3} [109]. Atomic coordinates from a well equilibrated melt from a building block [114] model (cooling rate of 0.1 K/fs) at 4000 K was taken as the starting model. This configuration was then refined iteratively with partial Reverse Monte Carlo (RMC) [44] and energy minimization carried out with conjugate gradient (CG) algorithm using the *ab initio* plane wave density functional theory package VASP [78] with projector augmented wave (PAW) [79] method and the Perdew-Burke-Ernzerhof (PBE) [80] treatment of the exchange-correlation functional. The *ab initio* minimization step in each FEAR iteration ensures that the interactions and chemistry are well represented, and the system does not produce chemically unrealistic structures which usually arise from conventional RMC. This process was repeated to produce five independent models with each of the annealed and as-deposited data, and the energy per atom on various models were within 2% of the average value. Each model, after the FEAR convergence, were relaxed with conjugate gradient relaxation in VASP until the system attains a DFT minimum of energy. After this relaxation, the final energies per atom in the as-deposited and annealed models were almost the same. In particular, it

would be interesting to get a measure of the difference between as-deposited and annealed models fitted to the two experimental results.

For validation and comparison purpose, we created a melt quench model of ZrO₂:Ta₂O₅ with 312 atoms. The final force/energy relaxed model showed weaker agreement with the experimental data for as-deposited films compared to the FEAR models. Since creating models of as deposited and annealed ZrO₂:Ta₂O₅ is rather complicated with traditional melt-quench (MQ), it would be difficult to study annealing induced changes with the MQ models. Although post treatment of MQ models to model annealing effects have been established and tested [115, 116], FEAR seems to be the go-to direction for our material.

Furthermore, x-ray scattering amplitude from a sample depends on the atomic number of the species present [117], therefore are less sensitive to O atoms relative to the Zr and Ta atoms. RMC alone with X-ray diffraction data could thus result in unexpected O behavior in such O rich stoichiometry. This shortcoming could be ameliorated by FEAR simulation technique where accurate interatomic potentials for each atomic species are used to refine the models.

The electronic structure of the models have been studied, in addition to usual PBE functional, using the Heyd, Scuseria and Ernzerhof (HSE06) hybrid functional [39, 85, 86] which has been quite successful in handling the DFT "band gap problem" and predicting optical properties. In this class of hybrid functional, the exchange potential is divided into short and long-range parts. For our system, we used the standard screening parameter ($\omega = 0.2$), with ω being related to the characteristic length, $2/\omega$, which defines the range separation. We have used default mixing parameters: 25% of the nonlocal Hartree-Fock exchange is mixed with 75% of the semilocal exchange in the generalized-gradient approximation of PBE [80]. The long-range part and the correlation

are determined using PBE. Also the ion-core and valence electron interactions were calculated with the PAW-potentials.

4.3 Results

4.3.1 Structural Properties

The structure factor S(Q), and the pair distribution function (PDF) obtained from the models are shown in Fig. 4.1, along with the experimental data for comparison. The results were averaged over five independent models for both the as-deposited and annealed data. Both as-deposited and annealed models agree reasonably well with the experiment. The PDF of both as deposited and annealed models show amorphous nature indicating that ZrO_2 :Ta₂O₅ does not crystallize upon 800°C annealing. As previously reported, this phenomena arises due the competing structural phases of zirconia interfering with the alignment of tantala polyhedra and thereby suppressing crystallization without generating a separate zirconia crystalline phase [118]. Additionally, Tewg *et al.* has also reported a 200°C increase in the amorphous-to-polycrystalline transition temperature of tantala with the right amount of zirconia doping [118].



Figure 4.1: Comparison of models with experiment: Experimental S(Q) and G(r) compared with that obtained from the models. The results are averaged over five models.

To understand the annealing induced changes in the structure, we plot the S(Q) and G(r) of as-deposited and annealed models together with the difference between them in Fig. 4.2. The differences in S(Q) is prominent at the first and second peak while the differences in G(r) manifest mostly in the region between 3 Å - 4 Å. This region of G(r) carries information regarding the connection of the various metal-oxygen polyhedra and therefore the figure suggests that annealing produces significant changes in these connections. The difference between the as-deposited and annealed models are subtle, and it is difficult to reliably pinpoint the differences in our models because the effects are so small. However, we calculated the standard error arising from the averaging over five

models and verified that the differences in the G(r) and S(Q) between the as-deposited and annealed models were higher than the error.



Figure 4.2: Comparison of as-deposited and annealed models: Comparison of S(Q) and G(r) from as-deposited and annealed models. The difference curve has been shown at the bottom.

To understand the real space correlations of the atoms, the structure of the material can be thought of as a collection of metal atom centered polyhedra with O atoms at the corners. The correlation between the metal and the O atoms within a polyhedra give rise to the first peak in G(r) at 2 Å. Metal-metal (M-M) correlation arising from different types of connection between the polyhedra, shown in Fig. 4.3 (left panel), give peaks in G(r) at different distances: edge-shared (ES) and face-shared (FS) connections combined show up as a peak at 3.5 Å while corner-shared (CS) connections give rise to a peak at 3.80 Å.

These findings are in good agreement with similar calculations made previously on zirconia-alloyed tantala [109] and on pure tantala [119, 120].

Fig. 4.3 (left panel) presents a comparison of G(r) from as-deposited and annealed models, with the lines thickened to show standard error. It shows that the M-O correlation is robust and unaltered by annealing. Low values of standard errors below 3 \mathring{A} in both as-deposited and annealed models show that all the models taken for averaging purpose had almost same M-O correlation in them. The M-M correlations, however, is modified significantly as a result of annealing. Annealed models tend to have a larger concentration of CS polyhedra and lower concentration of FS polyhedra compared to the as-deposited models. The comparison of different polyhedral connection shown on the right panel of Fig. 4.3 suggest that annealing increases the number of CS connections while decreasing the ES and FS connections between metal atoms in the network. As the measured room temperature mechanical loss of these thin films decrease upon annealing [109], this result supports the notion that TLSs contributing to the room temperature mechanical loss may involve ES and FS connection.



Figure 4.3: Effect of annealing in M-M correlation and polyhedra sharing fashion: (Left panel) Comparison of G(r) from as-deposited and annealed models. The curves are thickened to show the standard error present in the data. (**Right panel**) Comparison of the fraction of CS, ES, and FS polyhedra connections in the as-deposited and annealed models.

The bond angle distribution function obtained from the models has been shown in Fig. 4.4. The most obvious change in the bond angle occurs in the Ta-O-Ta connections. This increase in the peak around 130° for the annealed model is due to the increase in the CS Ta-Ta connections upon annealing. This finding has already been pointed out in our earlier work [109].



Figure 4.4: Bond angle distribution function for the as-deposited (dashed line) and annealed model (solid lines).

Model	Atoms	Та	0	Zr	Total
as-depo	Та		6.07		6.069 ± 0.038
	0	1.35		1.41	2.759 ± 0.003
	Zr		6.35		6.346±0.031
annealed	Та		5.90		5.896±0.031
	0	1.31		1.41	2.718±0.007
	Zr		6.34		6.342±0.053

Table 4.1: Coordination statistics for as-deposited and annealed models using 2.9 \AA M-O bond cut-off distance along with the fluctuations in the total coordination number over different models.

The coordination statistics of each atomic species are summarized in Table 4.1. The bond cut offs were taken from the first minima of the PDF and the coordination statistics are not too sensitive to this choice. Homopolar bonds are absent in all the as-deposited as well as annealed models and the only bonds present are the M-O bonds. The Ta-O coordination values for the as-deposited and annealed models are in agreement with results from NMR studies on pure Ta₂O₅ [121, 122]. Annealing did not produce a major change in the Zr-O coordination number but the Ta-O was significantly reduced as a result of annealing causing a major reduction in the O-Ta coordination number and the average O coordination by metal. As seen in Fig. 4.5, this reduction in O-M coordination number arises from a drop in fraction of 3- and 4- coordinated O atoms as a result of annealing. This finding is complemented by an increase in 5-fold Ta-atom due to annealing. Reduction in O coordination by metal upon annealing has previously been reported in similar measurements [109]. A significant change in Ta-O coordination compared to Zr-O upon annealing suggest that the Zr-O ionic bond is stronger than the Ta-O, a fact also backed up by their electronegativity values. The ratio of twofold to threefold coordinated O atoms in zirconia-alloyed tantala is $\sim 1 : 2$. Thus, zirconia doping modifies the bonding environment of oxygen significantly by producing more threefold coordinated O atoms in the network. Fig. 4.5 also shows that annealing reduces the fraction of higher coordinations across each species.



Figure 4.5: Change in coordination accruing from annealing.

The local environment around each atom is studied with Voronoi analysis. A Voronoi tesselation is defined by associating a cell of space to each atom that is closer to that atom than any other [123]. In general, a Voronoi cell for an atom can be constructed by drawing perpendicular bisector planes between the atom and its near neighbors.

The Voronoi radius (VR) for an atom can be obtained from the cell volume within the atomic sphere approximation that approximates the cell with a sphere equal to its volume. With this construction, atoms with closer neighbors distributed symmetrically have smaller Voronoi radius while atoms with neighbors further away have larger Voronoi radius. Furthermore, if an atom has a void near it, the Voronoi volume and hence radius is higher. Distribution of the VR in the sample has been shown in Fig. 4.6. The peak arising from Ta atoms is a clear signature of the Ta-O bonds because it is the shortest bond present in the network. The decrease in the peak height for Ta atoms upon annealing is a consequence of decrease in the O-Ta coordination. Since the range for the VR for Ta atoms is the smallest, the Ta atoms have the most compact nearest neighbor environment. Detailed analysis of the bonding environment showed that the tail of the Ta atoms are contributed by under coordinated (fivefold) Ta atoms while the lower end is contributed by over coordinated Ta atoms. Another peak due to Zr atoms lies in the intermediate region of O and Ta atoms because the bond length of Zr-O bonds is greater than that for Ta-O [109]. Low values of VR for both Zr and Ta atoms compared to O atoms highlight two key structural details of the models. First, the environment around metal atoms are more organized than the O atoms as most metal atoms from have a M-O polyhedral environment. Second, there is always an O atom closer to a void than any metal atoms. The VR associated with the oxygen atoms are the are the largest among the three which can be attributed to various factors. First, O atoms have the smallest number of nearest neighbors with no clear three dimensional picture of its environment: its neighbors are not arranged symmetrically. Secondly, they lie in the boundary separating voids and the dense matrix of atoms and have large unoccupied volumes included in their Voronoi cells.



Figure 4.6: Frequency distribution of Voronoi radius. The sum of the frequencies for each atom type is equal to the number of atoms of that particular type in the sample. The jagged oscillations are artifacts of the model size.

We begin by partitioning the system into large number of small spherical "cells" centered at the points of a $180 \times 180 \times 180$ grid and checking the distance of each sphere from all the atoms in the network. A cell is called "isolated" if it is further away than the covalent radius (1.70 Å for Ta, 0.73 Å for O, and 1.75 Å for Zr), plus a tolerance, from all the atoms in the network. We have used a tolerance of 0.9 Å in order to get rid of the inclusion of the cells lying along the M-O bonds, with a 2.90 Å cut-off, in the set of isolated cells. The collection of these isolated cells defines the region in real space in the network that is empty/void. We define void size as the combined volume of all the isolated cells within a void. The void sizes in the models are presented in Fig. 4.7. The fluctuations of void sizes among various models were within a few percent of the void size.The distribution of the void size shows that the as-deposited models, on average, have larger voids than the annealed models. The annealed models have a few large voids and a higher

fraction of uniformly sized smaller voids. Annealing thus annihilates the larger voids into smaller sizes which can be thought of as the bonded O atoms being pushed further from the metal atom thereby reducing the coordination, although subtly, as shown in Table. 4.1. This fact is also corroborated by the decrease in the fraction of highest coordinated metal atoms upon annealing, as seen in Fig. 4.5, which can be thought of as the O atom being pushed towards the void thereby annihilating the void. This is true not just for the 312-atoms models but also for the 2600-atom models.



Figure 4.7: Void size in the 416-atom (left) and 2600-atom (right) models. Both show annihilation of the voids upon annealing.

For visual interpretations, the voids present in one of the as-deposited and annealed FEAR models are shown in Fig. 4.8. It shows that voids in annealed sample is uniformly distributed and with a narrower range of sizes than the as-deposited models.



Figure 4.8: Distribution of voids in real space for as-deposited and annealed models . Different colors denote different voids in the system.

4.3.2 Optical and Electronic Properties

The frequency dependent complex dielectric function

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \tag{4.1}$$

for the as-deposited and annealed models were calculated within the projector augmented wave method where the imaginary part is derived by summing over conduction bands and the real part using Kramers-Kronig relation [124]. Both refraction and absorption of a medium can by described by a single quantity called complex refractive index defined as:

$$\tilde{n} = n + ik. \tag{4.2}$$

The real part is the normal refractive index while imaginary part is called the extinction coefficient and is directly proportional to the absorption coefficient of the medium. Both these quantities are calculated using the complex dielectric function with these definitions [125]:

$$n = \left(\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2}\right)^{\frac{1}{2}}, k = \left(\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2}\right)^{\frac{1}{2}}.$$
 (4.3)

The frequency dependence of the refractive index, calculated with the PBE and HSE06 functionals, has been shown in Fig. 4.9. The refractive index, for both as-deposited and annealed models, obtained using the hybrid functional (HSE-06) were much closer to the experimental results. The experimental value of the refractive index at 1064 nm is reported to be 2.08 ± 0.01 [107]. From Fig.4.9, the value calculated with HSE is much closer to the experimental value compared to that calculated with PBE.



Figure 4.9: Refractive index as a function of photon energy for as-deposited and annealed models.

The electronic density of state (EDoS) of the models evaluated with the Kohn-Sham eigenfunctions obtained from VASP using PBE and HSE06 hybrid functional have been plotted the results in Fig. 4.10. Since tantala is an insulator with a experimental band gap of 4.22 eV [126], introduction of zirconia (with band gap of 5.50 eV [127]) to the network does not change the insulating nature of the compound in contrast to the results seen in *Cu* doped tantala [128] where space projected conductivity calculations have shown that the

phase segregated *Cu* atoms form a conducting active region. The band gap observed in our models ($\approx 2.3 \text{ eV}$) calculated with PBE approximation is lower than reported, a discrepancy which can be associated with the well-known band-gap underestimation by DFT [129]. However, the band gap calculated with the hybrid functional (HSE06) shows a band gap $\approx 4 \text{ eV}$ which is close to the experimental band gap of tantala. The band gap for crystalline tantala and zirconia calculated using density functional calculations have been reported to be 2.2 eV [130] and 5.34 eV [131], respectively. Fig. 4.10 also shows that gap in the DoS is robust with respect to annealing.



Figure 4.10: Comparison of the electronic density of states (EDoS) between asdeposited and annealed models calculated using PBE (left panel) and HSE06 (right panel) approximations.

4.3.3 Vibrational Properties

The VDoS for the as-deposited and annealed models have been shown in Fig. 4.11. A detailed analysis of the contribution from individual atomic species showed the dominance of metal atoms at low frequencies while O atoms dominated the mid and high regions of the vibrational spectrum. The VDoS looks qualitatively similar in the as-deposited and the annealed models at low frequencies. However, there are certain regions where they differ significantly as we move higher in frequency, for example, near \approx 57.5 meV. The insets

show that the discrepancy arises because of the difference in the number of the vibrational modes present in the as-deposited and annealed models in that region.



Figure 4.11: (**left panel**) Vibrational density of states (arbitrary units) in as-deposited and annealed model. The insets show, in the energy range of interest, the energy associated with the normal modes in the as-deposited and annealed models. (**right panel**) Vibrational inverse participation ratio (VIPR), calculated for an as deposited model, projected onto different coordination of the O atoms.

The VIPR for the O atoms, decomposed onto different O coordination, is plotted in Fig.4.11. Low values of VIPR throughout the vibrational spectrum for the 4-fold O atoms indicate that the vibrational eigenmodes these set of atoms contribute to are highly delocalized. The normal modes towards the higher end of the spectrum are mostly localized on the twofold O atoms and on the threefold O atoms to some degree. A detailed investigation of these localized high frequency modes show that they are localized on a CS O atom connecting two M-O polyhedra and the vibrational mode is a bond stretch mode of the CS O atom between the two metal atoms. This localization at high frequency are important for thermal application because localized modes play a significant role in determining thermal conductivity in amorphous chalcogenides [132] and polymers [133].

4.4 Conclusions

New models of as deposited and annealed $ZrO_2:Ta_2O_5$ were created and models showed close agreement with the experimentally measured x-ray diffraction data. However, since the differences in G(r) and S(Q) are subtle, one must be careful in making sure that the errors in these functions are not greater than the difference between the as-deposited and annealed models. As deposited and annealed models of zirconia-alloyed tantala showed clear differences in structure in relation to the M-M correlations, coordination statistics, Voronoi radius, void size and distribution. Our models clearly capture the subtle differences in the experimental x-ray diffraction data for as-deposited and annealed samples that manifests mostly in the polyhedral linking fashions.

Annealing produced a prominent change in the coordination number of the Ta atoms. Further analysis of the Voronoi radius showed that there is always an O atom closer to a void boundary than any metal atom. The void distribution suggests a greater number of larger voids in as-deposited models compared to the annealed models. The electronic DoS shows that the insulating behavior of the host tantala is unchanged by annealing and zirconia doping. PBE functional calculations produce incorrect band gap for zr-alloyed tantala and the inclusion of hybrid functional to the DFT calculation in inevitable to get a good agreement with experimental results. The computational efficiency provided by FEAR helps us create 416-atom models, at DFT level, which would otherwise have been highly expensive using the traditional melt-quench method.

The results presented in this chapter provide an increased understanding of atomic structure of ZrO_2 :Ta₂O₅ coatings and the effect of annealing on the structure particularly in terms of polyhedral connection fashion – these results could be helpful to understand the origin of mechanical loss observed in these coatings so that coatings with lower losses, as needed for future generations of gravitational wave detectors, could be designed.

5 MEDIUM RANGE ORDER IN GE-SE GLASSES IN INTERMEDIATE PHASE

The work related to chalcogenide glasses presented in this chapter has been authored by **R. Thapa, C. Ugwumadu, K. Nepal, M. T. M. Shatnawi, and D. A. Drabold**, *Ab initio* simulation of amorphous GeSe₃ and GeSe₄, and submitted to JNCS, (2022) [8].

5.1 Introduction

Modeling of atomic-scale structure and ordering in amorphous materials has been an area of active research for decades now. It follows that an understanding of the basic architecture of a material creates an avenue for optimization of the material for wider applications. One material that has enjoyed tremendous scientific interest is the glassy Germanium Selenide materials, g-Ge_xSe_{1-x} ($0 \le x \le 1$). These materials can be made in glassy state over a wide range of x (0 < x < 0.43) [134], and reveal scientifically important ordering on the atomic scale [135-138]. This has also gathered a lot of attention because the connectivity of the covalently bonded network can be changed by altering the Ge:Se ratio over the glass forming region. Chalcogenide glasses are known to exhibit a wide range of physical properties like high linear and non-linear refractive indices, large infrared transparency, and reversible amorphous to crystalline transition [139]. GeSe₄ (x =(0.2) and GeSe₃ (x = 0.25) are important starting material in many opto-electronic applications, for example, purifying Se before glass synthesis of g-GeSe₄ fibres, used in optical telecommunication, notably reduces optical losses in the mid-IR range [140]. This property also extends to GeSe₃ which has low optical absorption due to its wide band-gap and configurable optical properties [141]. Using noble metals (notably Ag) as an additive to GeSe glasses forms a useful material for conducting bridge memory (CBRAM) devices, an ultra-low power non-volatile memory technology [142–144]. GeSe glasses
form an ideal system to study the floppy to rigid transition with an increase in the mean coordination as proposed by the constraint counting theory [145, 146]. As pointed out by Thorpe [147], the rigidity percolation occurs at a mean coordination of 2.4, corresponding to $GeSe_4$, where the network transforms from floppy to rigid with the transition being accompanied by abrupt changes in several physical properties [148–150].

For amorphous materials in general, accurate description of its vibrational, electronic and optical properties is heavily dependent on the availability of high quality structural models. For example, models generated solely from molecular dynamics (MD) not only suffer from short simulation times, but also produce unrealistic coordination defect concentration [12]. However, several sophisticated models for GeSe glasses exist which give better account of the structural properties of the material [4, 151–153], but the hybrid functionals used for those models are computationally expensive and most fail at reproducing the experimental Ge-Ge correlation function which is specified by the so-called first sharp diffraction peak (FSDP). For chalcogenide glasses with small Ge concentration, the Ge-Ge correlation function gives information on the Ge - centered structural motifs and hence contributes substantially to features of the model (i.e. from the exchange and correlation energy functional used [152, 154, 155] to the system size and residual pressure effects [1]). It is noteworthy that efforts are being made to improve the Ge-Ge correlation function, for example; Chaker and co-workers [156] incorporated Van der Waals dispersion forces into first-principle molecular dynamics simulations (FPMD) with BLYP (Becke, Lee, Yang and Parr) exchange-correlation functional [157, 158]; while this requires additional calculations, it showed that Ge-Ge correlation is sensitive to the kind of dispersion force considered. Therefore, since different conclusions can be inferred from the available models with regard to the network structure of g-GeSe₄ as well as g-GeSe₃ due to the inaccuracy in reproducing the Ge-Ge correlation function or some

other features, a break-through would be providing a model that can be consistent with all measured partial pair correlation function as well as experimental data.

The composition GeSe_4 is of special interest in the study of the floppy to rigid transition because this composition is the boundary between the two states, corresponding to mean coordination number 2.4 calculated with the 8-N rule [50]. Therefore, one might expect vibrational signatures to change significantly near this composition especially for the low frequency ($\omega \rightarrow 0$) limit. While the constraint counting theory is foundational contribution to our understanding of these materials, it is also idealized: it is based on a mean field theory and ignores forces other than stretching and bending forces from idealized bonds. In our work, we do not make these approximations, so that similarities and differences between the idealized and more realistic systems are of interest.

Several attempts to theoretically model the structure of GeSe₄ has been made in the past ranging from RMC simulations [137, 159–162] to classical molecular dynamics [163–165] to complex density functional theory based calculation with different exchange and correlation functional [4, 152, 156, 166]. An approach to simulating an acceptable model which can be used to explore structure-based properties of g-GeSe₄, as well as address the discrepancies between experiment and prediction of the Ge-Ge correlation function without using computationally expensive hybrid functional involves: (i) directly using available experimental information through the Reverse Monte Carlo (RMC) technique [44], (ii) a systematic minimization of the total energy of the configuration as well as the discrepancies in the atomic coordinates (caught by RMC) focused at increasing the probability of the system settling on a global minimum. This method of teaching some chemistry to the RMC is termed force enhanced atomic refinement (FEAR) [46, 48, 75]. In this work, we use x-ray diffraction (XRD) data [2] to construct realistic models for (g-GeSe₄) and (g-GeSe₃) and compare the results obtained with previous theoretical calculations and experiments whenever possible. The models

produced, in decent sizes, will be used to study the network topology in both the short and intermediate range.

5.2 Methodology and Models

We prepare models of GeSe₃ (384 atoms at 4.31 g/cm³ [1]) and GeSe₄ (400 atoms at 4.38 g/cm³ [167]) using FEAR [46–48]. FEAR is a well-developed method for generating computer models for a wide variety of materials ranging from *a* -Si and *a* -SiO₂ to sodium silicates [168] and complex bulk metallic glass [169]. Well-equilibrated liquid melts, at 2000 K for 10 ps, of the models generated using the *building block* [12, 114] method were used as starting configuration for the FEAR extrusively discussed elsewhere [46]. FEAR is a successful technique to jointly satisfy structure factor data while at the same time producing a configuration that is a suitable energy minimum according to VASP. The experimental structure factor used was measured using high energy X-ray diffraction carried out at the Advanced Photon Source (APS), Argonne National Laboratory [2]. The energy minimization step used conjugate gradient (CG) algorithm in the projector augmented wave [79] implementation of the *ab initio* plane wave density functional theory package VASP [78, 170] with Perdew-Burke-Ernzerhof [80] method as the exchange-correlation functional.

To compare/validate our findings from the FEAR models, we created a melt-quench (MQ) [12] models of the glasses with the same density using VASP. This model started with a random configuration of atoms, with no atoms closer than 2.0 \mathring{A} from other atoms, and was heated to 2000 K in 9 ps where it was equilibrated for 8 ps. The equilibrated melt was cooled to 300 K in 18 ps followed by a 12 ps equilibration at 300 K. The final models were then relaxed with CG algorithm to minimize the forces on each atom. Parallel FEAR calculations on smaller models (240 atom GeSe₄ and 300 atom GeSe₃) produced energy

optimized structures but the agreement with the experimental X-ray structure factor and the radial distribution function was not on the same level as with the larger models.

5.3 Results and Discussion

5.3.1 Structural Properties

The total structure factor obtained from the models is shown in Fig. 5.1, along with the experiment data [2] for comparison. FEAR models show modest agreement with the experimental results [2] and the most significant difference between the FEAR and the MQ models is the presence of a pre-peak at 1.15 $Å^{-1}$, although not matching the experimental intensity, in the FEAR model. This peak is the first sharp diffraction peak (FSDP) and is related to ordering of atoms in the intermediate range [1, 171]. Since, this FSDP arises mainly from the Ge-Ge correlations [1], a FSDP mismatch of the model with the experiment results in wrong Ge-Ge correlations as seen in the RDF of the MQ model. The comparison of total neutron structure factor obtained from the model with the experimental data [1], shown in Fig. 5.2, also shows that the FEAR models align closer to the experiment compared to the MQ models, markedly in the region around the FSDP.



Figure 5.1: Total x-ray structure factor of the MQ and FEAR models of GeSe3 (left panel) and GeSe4 (right panel) compared with experimental results from Moneeb *et. al* [2].

The total and partial RDF were calculated on both the FEAR and MQ models. To serve this purpose, the models were taken through an NVT ensemble at 300 K and the results were averaged over 2500 configurations collected over the final 5 ps of the simulation. The partial and total RDF from our models, plotted in Fig. 5.4, are in close agreement with the experimental results obtained using neturon diffraction with isotope substitution [1]. The absence of Ge-Ge homopolar bonds (correlations below $3^{\text{Å}}$) in GeSe₄ observed in the neutron diffraction experiment [1] is exactly reproduced in our GeSe₄ model. The position of the peaks in the partial RDF and the mean coordination number, outlined in Table. 5.1 agree with available experiments.



Figure 5.2: Total neutron structure factor of the MQ and FEAR models of GeSe3 (left panel) and GeSe4 (right panel) compared with experimental results from Rowlands *et*. *al* [1].



Figure 5.4: Partial radial distribution function of the MQ and FEAR models of GeSe₃ (left panel) and GeSe₄ (right panel). The RDF's have been shifted vertically for clarity.



Figure 5.3: Projection of the localized states near the Fermi level onto atoms in $GeSe_3$ (left) and $GeSe_4$ (right) models. Red and green atoms indicate Ge and Se atoms respectively. Only few atoms with higher projection of the states on them are shown.

In general, the models produce reasonable agreement with the experiment in terms of the Ge-Se and Se-Se correlations. However, the Ge-Ge correlations, which is highly sensitive to the choice of the modeling procedure, differ between the MQ and FEAR models. The dependence of the Ge-Ge correlations on the exchange and correlation energy functional used in the simulations [154, 155], the system size, and the quench protocol used [153, 172] have been previously reported. This absence of Ge-Ge correlations in GeSe₄, also observed experimentally [1], indicates the absence of Ge-Ge homo-polar bonds, i.e. Ge atoms bond only to Se atoms. The first peak in the total RDF of GeSe₄ arises from first neighbor correlations between the atoms within a structural motif. Thus, Fig. 5.4 suggests that there is no Ge-Ge correlations in GeSe₄ model for the FEAR model but such a correlation exists for the MQ model. This finding also accounts for the discrepancy in the intensity of the first peak between the MQ and FEAR models of GeSe₄. Experimental evidences have shown that there is no Ge-Ge correlations in GeSe₄ [1].

The structure of GeSe₃ and GeSe₄ can be viewed as a collection of Ge centered tetrahedra connected to each other by Se atoms in various fashion namely edge shared (ES) and corner shared (CS). The frequency of occurrence of Se-Se homo-polar bonds and the length of Se chains positively correlates with the Se concentration. Our models for GeSe₃ and GeSe₄ show four distinct Se environments: Ge-Se-Se, Se-Se-Se, and Ge-Se-Ge where the Se atom is shared by two $Ge(Se)_4$ tetrahedra connected either in CS or ES fashion. This finding is in line with NMR experiments on these materials [173]. The comparison of real and reciprocal space information for GeSe₃ and GeSe₄ shows that an increase in Ge-Se content within the intermediate phase (IP) creates an additional length scale in the atomic ordering associated with the intermediate range order arising from the connection of Ge atoms in neighboring tetrahedra [174]. This manifests as a peak in the Ge-Ge correlation in the GeSe₃ and as a FSDP, with higher intensity compared to $GeSe_4$, in the S(Q). To study the difference in the Ge-Ge connectivity between GeSe₃ and GeSe₄, we calculated the statistics of the different modes of connections between the Ge-centered motifs: namely corner-shared and edge-shared, and tabulated in Table. 5.2. The table shows a significant increase in the connectivity between Ge-atoms, both CS and ES, as we go from GeSe₄ to GeSe₃. This can be thought of as the added Ge atoms trying to break up and crosslink the Se chain structures by forming fourfold coordinated Ge-centered structural motifs [174]. Also, the ratio of ES:CS tetrahedra in GeSe₃ is in close agreement with results from MAS NMR experiment [173]. The frequency of the length of most frequent isolated Se chains, made with Se atoms that are not bonded to Ge, listed in Table. 5.2 suggests that the addition of Ge atoms to GeSe₄ breaks the Se chain links to form cross-linking connections and a more rigid network topology. he number of Ge-Ge

	GeSe ₃	GeSe ₄		
R _{GeGe}	2.55			
R _{GeSe}	2.42 (2.37)	2.44 (2.37)		
R_{SeSe}	2.40 (2.34)	2.37 (2.35)		
n	2.50	2.38		
<i>ī</i> n (8-N)	2.50	2.40		

bonds reported in Table II for GeSe4 agrees well with the Ge-Ge coordination number reported in Rowlands et al. [26].

Table 5.1: Position of the first peak ($R_{\alpha\beta}$) (in Å) in partial correlations calculated from FEAR models of GeSe₃ and GeSe₄. The quantities in the brackets are taken from neutron diffraction study by Rowlands *et. al* [1]. The average coordination number (\bar{n}) for each model is also listed.

The atomic correlation further than the nearest neighbor was analyzed on the CG relaxed models using the ring statistics algorithm that has been applied to both compositions using the ISAACS code. The bond cutoff distances between atomic pairs are determined by the first minima of the partial RDF and are different for GeSe₃ and GeSe₄. Within ISAACS, we used the algorithm developed by King [175] and later updated by Franzblau [176]. As seen in Fig. 5.5, there is a significant difference in the distribution of the rings between the two compositions. These results are in significant agreement with previous DFT calculations [4]. The increase in the number of 4-fold rings in GeSe₃ is attributed to the higher fraction of ES Ge(Se)₄ tetrahedral connections compared to GeSe₄.

The bond angle distribution (BAD) is also studied to understand the local structure around the $Ge(Se)_4$ tetrehedra and the way they are connected. The Se-Ge-Se BAD is peaked at around 110° indicating the presence of tetrahedral order [4]. The Ge-Se-Ge

	GeSe ₃ GeSe			
CS	1.030	0.750		
ES	0.135	0.125		
n _{GeGe}	14	0		
n_{Se_4}	9	13		
n_{Se_5}	6	8		
n_{Se_6}	1	3		

Table 5.2: Statistics of the Ge-Ge connectivity in GeSe₃ and GeSe₄ calculated using Ge-Se bond length of 2.90 Å. Ge atoms are considered bonded if they are less than 2.90 Å apart. The number of ES, CS connections are normalized by the number of Ge-atoms in the models. The number of the most frequent isolated Se-chains with different lengths n_{Se_n} is also listed.

BAD, arising from connection between the tetrahedra, has clear peaks at $\sim 80^{\circ}$ and $\sim 100^{\circ}$ assigned to ES and CS tetrahedra, respectively. The intensity of the ES peak appears to be inversely proportional to the Ge content as previously observed [4]. This dominance of ES units is larger in GeSe₃ which can also be seen from the ring statistics.





Figure 5.5: Distribution of rings of different size in the models. Bond cutoff are taken from the first minimum of RDF.

Figure 5.6: Bond angle distributions in the models computed for Ge-Se-Ge and Se-Ge-Se. The BAD has been Gaussian broadened (with $\sigma = 2.5^{\circ}$).

5.3.2 Electronic Properties

From Fig. 5.7, we observe that our models have low DoS near the Fermi level, consistent with previous experiments [3] and simulation results [4]. Furthermore those states are highly localized, as suggested by higher values of IPR. The combined effect of these findings suggests that the models are non-conducting. Furthermore, the partial DoS plots show that the significant contribution to the DoS comes from the Se atoms in both models. In order to understand the origin of the localized states near the Fermi level, we show the atomic projection of four such states onto the atoms in Fig. 5.3. As expected for localized states, the states are highly localized on few atoms. Furthermore, these localized states arise mostly from the Se chain links in the network which is also seen in the partial DoS in Fig. 5.7.



Figure 5.7: Total and partial Electronic DoS and Inverse Participation Ratio (IPR) calculated for $GeSe_3$ (left) and $GeSe_4$ (right) models. The results are compared with photoemission spectroscopy (red circles) [3] and previous simulation result (red triangle) [4].

The total and partial VDoS plotted in Fig. 5.8 agree reasonably well with previous calculations on the materials [4, 177] showing a broad band centered at ~ 80 cm⁻¹ for both models and matching subsequent peak positions. The low frequency peak at ~ 50 cm⁻¹ arises mainly from the floppy modes arising from the vibrations among the loosely bound Se-atoms. As suggested by VIPR, these low frequency floppy modes are highly delocalized and shared by a large number of Se-atoms. Sub peaks at ~ 160 cm⁻¹ and ~ 250 cm⁻¹, arising from bond-bending and bond stretching vibrational modes respectively,

have been previously reported [177]. The Se rich $GeSe_4$ has a higher intensity of the high frequency motion associated with the A_{1c} mode arising from the atomic motion of Se atoms connecting edge-shared tetrahedra [178]. This can be viewed as an effect of increased concentration of the ES tetrahedral connection in $GeSe_4$ compared to $GeSe_3$, a finding also seen in the ring statistics analysis above. To facilitate a visual interpretation of the different kinds of vibrational modes present in the system, we have included animations of representative modes along with this manuscript.



Figure 5.8: Total and partial VDoS and VIPR calculated for GeSe₃ (left) and GeSe₄ (right) models.

5.4 Conclusion

We generated realistic models of GeSe glasses in the intermediate range using experimental x-ray diffraction measurements. The models produced showed good agreement with the experiment even without the use of hybrid functional calculations. The structural, electronic, and vibrational signature of the models were parallel with previous theoretical and experimental studies. The Ge-Ge correlations in these glasses matched significantly well with experiments. This is a clear advantage of the FEAR over the MQ technique because FEAR injects the experimental information into the model in each step. As we moved from GeSe₄ to GeSe₃, we saw clear signature of breaking of Se chains and formation of cross-linking connections to form a more rigid topology.

6 CONDUCTING CHANNEL IN AN INSULATING MATERIAL

The work related to Cu doped tantala, presented in this chapter has been published as **R. Thapa, B. Bhattarai, M. N. Kozicki, K. N. Subedi, and D. A. Drabold**, Structure and charge transport of amorphous Cu-doped Ta₂O₅: An ab initio study, Phys. Rev. Mater. **4**, 064603 (2020) [128].

6.1 Introduction

Novel non-volatile memory devices are an area of active inquiry. Research on ferroelectric random access memory (FeRAM) and magnetoresistive random access memory (MRAM) have been limited due to underlying technological and scalability problems [179]. Meanwhile, study of non-volatile memory, based on electrically switchable resistance or resistive random access memory (ReRAM), has gained considerable interest. The first studies of such resistive switching was reported in the 1960's and was based on oxides in a metal-ion-metal (MIM) framework with formation/dissolution (SET/RESET) of filament electrochemical in nature [180]. Amongst ReRAM's, electrochemical metallization mechanism (ECM) or conductive bridging random access memory (CBRAM) which utilizes the electrochemical dissolution of an active electrode material such as Cu or Ag for SET/RESET mechanism has shown particular promise. In CBRAM, transition metals in their ionic state are converted to a conducting filament by applying a suitable electric field, which upon reversal, destroys the filament resulting in a resistive state. Several possible candidates for solid electrolytes have been studied elsewhere [181–186]. Amorphous tantalum pentoxide/amorphous tantala (a-tantala) has been investigated as a possible candidate for memory devices, anti-reflection coatings and optical waveguides due to its high dielectric constant, high refractive index, chemical and thermal stability [109, 187, 188]. Cu-doped a-tantala shows promising properties for CBRAM based memory devices.

Several experiments as well as calculations [189–192] have been carried out to understand conduction mechanisms in tantala materials. In these studies [189, 191, 192], *Ag*, *Cu*, *Pt* metals were used as electrodes while in one Xiao *et. al.* [190] used Cu nanowires of different diameters inserted into the low density tantala host to study transport and electronic properties of tantala as an electrolyte. These papers indicate that metal filaments are responsible for conduction. It has been reported that conduction paths in different electrolytes differ qualitatively. Metals such as Cu form clusters, leading to a conducting filament in oxides, while no such clustering is observed in chalcogenide based electrolytes [193]. Since a complete investigation of Cu-doped tantala has not yet been reported, we provide here a thorough investigation amid growing research to test its candidacy as a possible electrolyte for CBRAM technologies.

In this chapter, we investigate the structural, electronic and lattice dynamics of amorphous Cu -doped a-tantala. We provide insights into structural properties and coordination statistics, electronic and vibrational properties, and visualize conduction/current paths by computing the space-projected conductivity (SPC) [193]. We elucidate the atomistic mechanisms of phase segregation and track the emergence of Cu clusters as the melt cools.

6.2 Methodology and Models

We prepare two 210-atom models of a- $(Ta_2O_5)_{0.80}Cu_{0.20}$ cooled at different rates by utilizing melt-quenching within the *ab initio* molecular dynamics (AIMD) method. The initial density for both of the models was chosen to be that of amorphous tantala ($\rho = 7.79$ g/cm³), consistent with experimental [194, 195] and theoretical studies [190]. We have performed molecular dynamics simulations using *ab initio* plane wave code VASP [78, 170] with projector-augmented wave (PAW) method [79] and employed the *Perdew-Burke-Ernzerhof* (PBE) [80] exchange-correlation functional. Due to the size of



Figure 6.1: (a) The structure of Model I (a) and Model II (b) consists of tantalum atoms bonded to 5, 6 and 7 oxygen atoms to form a mixture of edge-sharing, corner-sharing and face-sharing polyhedra and a connected sub-network of Cu atoms. The Cu network grows in the interstitial space between Ta-O polyhedra. Cu , Ta and O atoms are shown in blue, green and red, respectively and the same "color nomenclature" will be used throughout the chapter.

the unit cell, only the Γ -point is used for Brillouin zone (BZ) integration. A plane-wave cut off of 500 eV, a time step of 3.0 fs and Nose' thermostat was used to control the temperature.

We fabricated a starting model of 48 Ta, 120 O and 42 Cu atoms with random initial positions (with no atoms closer than 2 Å) in a cubic box of side 14.14 Å. This model was then taken through a *melt quench* (MQ) [12] cycle. Firstly, the system was heated well above melting point to form a liquid at 6000 K and then equilibrated at 6000 K, cooled to 3000 K in 18 ps, equilibrated at 3000 K for 9 ps and further cooled to 300 K in 15 ps summing up for a total simulation time of 57 ps. The cell volume was relaxed to obtain

zero pressure models. This zero-pressure relaxation produced a volume rise of 2.09% yielding an optimized density of 7.63 g/cm³.

Another melt and quench (MQ) model, with slower cooling rate around the melting point of tantala, was made. This model started with the melt of Model I cooled to 3000 K and was further cooled to 300 K in 24 ps without any intermediate equilibration. The total simulation time was 60 ps.

After dynamical arrest, conjugate-gradient relaxation was applied until the magnitude of the force on each atom was reduced to less than 0.01 eV/Å. Zero-pressure relaxation increased the volume by 2.39% and the density was optimized to 7.61 g/cm³.

For simplicity and consistency, we follow the same "color nomenclature" for the atomic species: Ta , O , and Cu atoms are colored green, red, and blue respectively.

6.3 Results

Fig. 6.1 suggests the formation of Cu clusters within the network of amorphous tantala. This can be attributed to the ionicity of the Ta -O bonds [196] that drives the Cu-atoms to cluster. Clustering of Cu in ionic host (a-Al₂O₃) has been previously reported [193]. This strong Cu-Cu correlation suggests that Cu-atoms preferentially bond with themselves, consistent with the coordination statistics in Table 6.1. In contrast, zirconia-doped tanatala shows no Zr clustering and, the metal atoms distribute themselves homogeneously with no metal-metal pair closer than 2.9 Å [109]. It is quite interesting that our calculations "naturally" produce connected Cu "wires" that are extended in space (considering the periodic boundary conditions), not by modeler's "installation", but as a direct and unbiased consequence of the melt-quench simulations themselves.

Two peaks are worth mentioning in the Ta-Ta correlation: the first at around 3.3 Å, and the second around 3.8 Å, firstly because they provide an idea of the how the Ta-O octahedra are connected, and secondly because they are implicated in mechanical loss for

	Atom	n	n(Ta)	n(O)	n(Cu)
ModelI	Та	7.96	1.75	5.52	0.69
	0	2.44	2.21	0.00	0.23
	Си	7.17	0.79	0.67	5.71
ModelII	Та	8.00	1.92	5.60	0.48
	0	2.45	2.24	0.00	0.21
	Си	7.48	0.55	0.60	6.33

Table 6.1: Average coordination number (*n*) and its distribution among different species. Coordination is counted only if the distance between the atoms is no more than the sum of their covalent radius within a tolerance of 0.1 Å. Covalent radii for Ta, O and Cu are taken as 1.70 Å, 0.73 Å, and 1.32 Å, respectively

Laser Interferometer Gravity Wave Observatory application [109]. The former comes from the joint contribution of face and edge-shared octahedral connection while the latter derives from the corner-shared connection of the octahedra.

The coordination statistics of the models in Table I largely serve to validate the findings of the RDF and the correlations between different species. It also suggests that, as we lower the cooling rate, the Cu-Cu coordination increases while the Cu-O coordination decreases. This implies slower cooling rates produce better Cu clusters with O being pushed away from them.

To compare the Cu-Cu and the Cu-O environment and its evolution during the *melt and quench* process in our models, we calculate, at each step, the following quantities:

$$d_{CuCu} = \frac{1}{3N_{Cu}} \sum_{i=1}^{N_{Cu}} \sum_{j=1}^{3} |\vec{R}_{Cu,i} - \vec{R}_{Cu,j}|$$
(6.1)



Figure 6.2: Average distance of three nearest Cu to Cu atoms (blue dots) and O to Cu atoms (purple dots), averaged over all Cu atoms, for Model I (**a**) and Model II (**b**).

$$d_{CuO} = \frac{1}{3N_{Cu}} \sum_{i=1}^{N_{Cu}} \sum_{j=1}^{3} |\vec{R}_{Cu,i} - \vec{R}_{O,j}|$$
(6.2)

The sum over *j* runs over three nearest Cu in the first equation and over three nearest O in the second. The scatter plots in Fig. 6.2 show how these distances change as we cool the melt. This plot clearly shows that as we reduce the cooling rates, the O and Cu atoms move apart. Furthermore, the details of the change in the bonding environments of the atoms and the phase segregation of Cu atoms in the network during the *melt and quench* process has been discussed with animations in the Supplementary Material. There, we provide a visualization of the network formation process, and observe the exclusion of Cu as the host tantala network, rendering the Cu becomes *atomus non grata* in or near the tantala regions. The main "takeaway" from Fig. 6.2 is that the more extended cooling produces a more compact Cu cluster for Model II (hence the extended right "leg" on the right side of the "ballerina plot" of Fig. 6.2b compared to Fig. 6.2a). This suggests that slower cooling rates create Cu clusters that are as compact as possible, and minimize Cu

cluster surface area exposed to the tantala host. Of course this hints at a propensity to form crudely spherical clusters, though our simulations are too small to prove this assertion.



Figure 6.3: Electronic density of (Kohn-Sham) states, Inverse Participation Ratio and projection onto atomic species for Model I (**a**) and Model II (**b**) with black vertical drop lines indicating Fermi level. The insets show a magnified version of the DoS contributions from each species near the Fermi Level.

To understand the electronic structure of the models, we examine the total density of states (DoS), partial DoS and inverse participation ratio (IPR). These calculations not only help us check the validity of the model, but can also be used for *a priori* information to

model amorphous materials [197, 198]. The plot of the DoS in Fig. 6.3 reveals that both models have states around the Fermi level with extended Kohn-Sham orbitals indicating conducting behavior. Since the host (tantala) is an insulator with a band gap of 4.22 eV [199], we see that the introduction of Cu to the network closes the gap by inducing impurity bands spread throughout the *entire* host (tantala) gap. This is corroborated by the fact that the states near the Fermi level arise from the Cu -3d orbitals hybridized mainly with Ta and small contributions from O orbitals, as seen in the partial DoS plots in Fig. 6.3.

The density of states provides some hints about the species contributing near the Fermi-level; however, the conduction also depends upon the localization of their electronic states and momentum matrix elements between Kohn-Sham states near the Fermi level. Recently, we have developed a spatial decomposition of the Kubo-Greenwood [200, 201] formula that provides information about conducting paths in real space. By introducing a discrete grid in space, we show that the quantity:

$$\zeta(\mathbf{x}) = \left| \sum_{\mathbf{x}'} \Gamma(\mathbf{x}, \mathbf{x}') \right|$$
(6.3)

provides such information at the spatial grid point \mathbf{x} and for which:

$$\Gamma(\mathbf{x}, \mathbf{x}') = \sum_{ij\alpha} g_{ij} \xi^{\alpha}_{ij}(\mathbf{x}) (\xi^{\alpha}_{ij}(\mathbf{x}'))^*.$$
(6.4)

Here, g_{ij} is defined in *Prasai et. al* [193] and $\xi^{\alpha}_{ij}(\mathbf{x}) \equiv \psi^*_i(\mathbf{x})p^{\alpha}\psi_j(\mathbf{x})$ is a complex-valued function, $\psi_i(\mathbf{x})$ is the *i*th Kohn-Sham eigenfunction and $p^{\alpha} = \frac{\hbar}{i} \frac{\partial}{\partial x_{\alpha}}$, ($\alpha = x, y, z$). We have used this approach to describe transport in a solid electrolyte material [193] and Cu -doped *a*-alumina [202]. In a mixed (insulating/conducting) system like ours only a few eigenvectors of Γ characterize essentially all conduction in the system.

The SPC for both models is visualized as a gray-scale plot in Fig. 6.4. The figure shows that connected Cu atoms form primary sites of conduction as expected. However,

some Ta atoms, which are near the Cu atoms also contribute significantly to the electronic conduction. A detailed analysis of the bonding environment of these Ta atoms show that they are under-coordinated with oxygen, i.e. have less than (or equal to) five O bonds, a result that in agreement with previous works on non-stoichiometric tantala [203]. A detailed discussion of the bonding environment and the coordination statistics of these Ta atoms has been made in the Supplementary Material. Furthermore, slower cooling rates produces higher Cu-Cu coordination and better connectivity, thereby enhancing conductivity. There is a factor of about 5 higher conduction in Model II than Model I, presumably because of the small "neck" interlinking Cu in Model I.



Figure 6.4: Space Projected Conductivity scalar field for Model I (**a**) and Model II (**b**) shown in gray scale. Those parts of the network containing the interlinked Cu-atoms are clearly more conducting in both models. The electrical conductivity of Model II is about 5 times that of Model I, because of the more robust Cu filament of Model II.

6.4 Conclusion

We describe the process of phase segregation of Cu in a-tantala in atomistic detail. The Cu did not significantly alter the Ta-O bonding but instead phase separated, forming Cu clusters. Models made with a slower cooling rate revealed significantly better (denser) clustering compared to the one with faster cooling rate. These clusters, along with the neighboring under-coordinated Ta atoms, form a conducting path in the network which is in agreement with previous literature, though presented in novel way in this chapter, and not relying only on the Kohn-Sham states near the Fermi level, but also the momentum matrix elements, a legacy of the current-current correlation functions of Kubo. All this lends significant insight into an important CBRAM material.

It is interesting to speculate on what would happen in larger models and different cooling rates. We might expect to see Cu blobs in the network, possibly spatially separated but potentially interconnected by some other conducting fabric, perhaps Cu nanowires (of essential interest of course for CBRAM applications). While direct simulations like this one is computationally impossible for so large a system, it provides potentially useful *a priori* information for modeling employing simpler interatomic interactions. Electronic DoS calculations show that Cu-doping closes the gap in the DoS of pure a-tantala with extended Kohn-Sham orbitals around the Fermi level.

7 CONCLUSIONS

We have extended and applied a successfully established method of incorporating experimental diffraction data as input into MD simulations coupled with *ab initio* electronic structure minimization to generate models of amorphous materials of technological and scientific importance. Using FEAR, we tracked down the structural changes in the metal-oxygen (M-O) polyhderal connections as a function of annealing which would have otherwise been impossible with other traditional modeling techniques like melt-quench (MQ) or Reverse Monte Carlo (RMC). Annealed models had a higher fraction of corner-shared (CS) connections compared to the as deposited models, a finding in close agreement to the experiment and previous theoretical calculations. The method was then improved further to understand the structural differences between chalcogenide glasses in the intermediate range. The results were in close agreement with experimental diffraction data and produced structural characteristics with minimum computational effort that would have previously required highly-expensive hybrid calculations.

We undertook a pioneering study of graphitization of non-crystalline carbon materials under high temperature annealing using *ab initio* MD simulations as well as ML potentials. The annealed structure had an unusually high proclivity towards layering with interlayer separations close to that of graphite. Each individual layer of a-G is an amorphous graphene with topological ring disorder. We studied the effect of the disorder on the electronic conduction, charge distribution, and interlayer binding.

In an effort to understand Conducting Bridge Random Access Memory (CBRAM) devices, we studied the formation of connected network of Cu atoms in an insulating host using *ab initio* simulation. The findings showed that quenching a high temperature melt of the mixture of Ta_2O_5 and Cu causes the Cu atoms to cluster within a growing network of amorphous Ta_2O_5 . Multiple simulations on different time scale showed that the extent of clustering was a increasing function of the simulation time. The analysis of the electronic

properties using density of states (DoS) and space projected conductivity (SPC) showed that the Cu cluster formed a conducting channel within the insulating host.

7.1 Future Work

Our work on temperature induced structural transition of non-crystalline carbon has added a dimension to the widely research graphitization process. Experimental researchers could try to exfoliate the graphite obtained from graphitization to compare and contrast with the individual layers of the simulated a-G. This study of transformation from a disordered phase to a more ordered phase under the effect of high temperature is of technological importance in different class of materials.

The annealing induced rise in the fraction of sp atoms, crucial for improving the electrical conductivity of amorphous carbon materials, could be quantified by further electronic conductivity calculations (e.g. SPC). This could be extended to produce electronic applications of the non-crystalline carbonaceous materials discussed in this dissertation. The methods implemented in this dissertation to understand the structure and properties of C-foam could be extended further. The foaming algorithm developed herein could be extended to large models with million of atoms which could produce foam models 50-100 \mathring{A} in size. Such large systems would require ML potentials, which are already available, and high performance computing (HPC) resources. Structural changes under annealing at low temperatures (< 1500 K), experimentally known to produce significant changes in electronic conduction, could be studied with these large foam models.

The FEAR simulation protocol can be extended further with the incorporation of linear scaling ML potentials in the energy minimization step. This allows us to work on model with millions of atoms thereby generating a more realistic picture of the material being studied. FEAR simulation on large models could reveal technologically important information not known to the community yet because, by construction, the technique incorporates experimental information into the system while also minimizing the energy of the system with a high-quality interatomic interaction. Our technique to study the formation of conducting channel in an insulating host could be extended to a wide variety of the CBRAM memory materials.

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Appendix: Dedication



Dedicated, in loving memory, to my dad.



Thesis and Dissertation Services