

MULTISCALE MODELING OF CHALCOGENIDES

BY

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Abstract

Chalcogenide glasses exhibit properties applicable to a wide range of fields, including electrical and optical switching and the transmission of infrared radiation. In this thesis, we adopt a hierarchical multiscale modeling approach to investigate the fundamental physics of chalcogenide systems.

Our multiscale modeling begins in Part I at the quantum mechanical level, where we use the highly accurate Møller-Plesset perturbation technique to derive interaction potentials for elemental and heterogeneous chalcogenide systems. The resulting potentials consist of two-, three-, and effective four-body terms.

In Part II, we use these *ab initio* derived potentials in classical Monte Carlo simulations to investigate the structure of chalcogenide glasses. We discuss our simulation results in relation to the Phillips model of topological constraints, which predicts critical behavior in chalcogenide systems as a function of average coordination number.

Lastly, in Part III we address the issue of glass transition range behavior. After reviewing previous models of the glass transition, we derive a new model based on nonequilibrium statistical mechanics and an energy landscape formalism. The new model requires as input a description of inherent structure energies and the transition energies between these structures. To address this issue, we derive an eigenvector-following technique for mapping a multidimensional potential energy landscape. This technique is then extended for application to enthalpy landscapes. Our model will enable the first-ever calculation of glass transition behavior based on only *ab initio* derived physics.

Part I

Quantum Mechanics

Chapter 1

Many-Body Quantum Theory

1.1 Overview

Chalcogenide glasses exhibit unique electrical and optical properties applicable to a wide range of fields, including electrical and optical switching and the transmission of infrared radiation. However, these glasses must meet requirements for thermal and mechanical properties such as glass transition temperature, strength, and toughness in order to be suitable for many applications. Experiments have shown the promising but often puzzling behavior of various chalcogenide glass compositions, but there is yet to be a thorough investigation of chalcogenides based on first principles. In this thesis, we adopt a hierarchical multiscale modeling approach to investigate the fundamental physics of chalcogenide systems.

A schematic diagram of our multiscale approach is shown in Figure 1.1. We begin at the quantum mechanical level, where individual electrons and nuclei are the fundamental units under study. At this level, we use the highly accurate Møller-Plesset perturbation

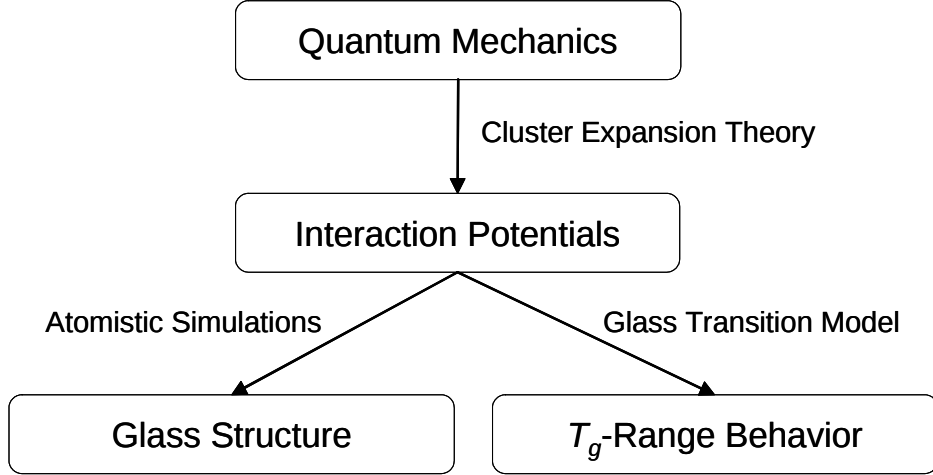


Figure 1.1. Schematic diagram of our multiscale modeling approach.

technique to derive interaction potentials for elemental and heterogeneous chalcogenide systems. We begin by simulating elemental sulfur, selenium, tellurium, arsenic, and germanium, and then proceed to binary and ternary systems. A cluster expansion approach is used to isolate contributions due to two-, three-, and higher-body effects.

These *ab initio* potentials are then used in classical atomistic simulations to characterize the structure of several chalcogenide systems, including S, Se, Te, S-Se, Se-Te, Ge-Se, As-Se, and Ge-As-Se. The model potentials are shown to successfully reproduce experimental structural data, including pair distribution functions and coordination number distributions. Our simulations also give support for a rigidity percolation threshold in the Ge-Se and As-Se systems. Our work is the first to derive explicit interatomic potentials from *ab initio* simulations for chalcogenide systems. It is also the first to bridge the gap between quantum and classical simulations for chalcogenide systems, offering a true multiscale approach that combines the accuracy of quantum computations with the size and efficiency of classical simulation techniques. Our approach is shown to provide advantage

over traditional modeling using semi-empirical and density functional methods.

Finally, we address the issue of glass transition range behavior. After reviewing previous models of the glass transition, we derive a new model based on nonequilibrium statistical mechanics and an energy landscape formalism. The new model requires as input a description of inherent structure energies and the transition energies between these structures. To address this issue, we derive an eigenvector-following technique for mapping a multidimensional potential energy landscape. This technique is then extended for application to enthalpy landscapes. Our model will enable the first-ever calculation of glass transition behavior based on only *ab initio* physics.

Some of the work presented in this thesis has been published in the following journal articles:

- J.C. Mauro and A.K. Varshneya, "Modeling of Selenium Telluride Glass," *Phys. Status Solidi B*, **242** [6] R46-8 (2005).
- J.C. Mauro and A.K. Varshneya, "Model Interaction Potentials for Selenium from *Ab Initio* Molecular Simulations," *Phys. Rev. B*, **71**, 214105 (2005).
- J.C. Mauro and A.K. Varshneya, "Monte Carlo Simulation of $\text{Se}_x\text{Te}_{1-x}$ Glass Structure with *Ab Initio* Potentials," *Phys. Rev. B*, **72**, 024212 (2005).
- J.C. Mauro, R.J. Loucks, and J. Balakrishnan, "A Simplified Eigenvector-Following Technique for Locating Transition Points in an Energy Landscape," *J. Phys. Chem. A*, **109** [42] 9578-83 (2005).
- J.C. Mauro and A.K. Varshneya, "A Nonequilibrium Statistical Mechanical Model of Structural Relaxation in Glass," *J. Am. Ceram. Soc.*, **89** [3] 1091-4 (2006).
- J.C. Mauro and A.K. Varshneya, "*Ab Initio* Modeling of Glasses in the Sulfur-Selenium System," *Am. Ceram. Soc. Trans.*, in press (2006).
- J.C. Mauro, R.J. Loucks, and J. Balakrishnan, "Split-Step Eigenvector-Following Technique for Exploring Enthalpy Landscapes at Absolute Zero," *J. Phys. Chem. B*, **110** [10] 5005-11 (2006).

- J.C. Mauro, R.J. Loucks, J. Balakrishnan, and A.K. Varshneya, “Potential Energy Landscapes of Elemental and Heterogeneous Chalcogen Clusters,” *Phys. Rev. A*, **73**, 023202 (2006).
- J.C. Mauro and A.K. Varshneya, “Multiscale Modeling of GeSe₂ Glass Structure,” *J. Am. Ceram. Soc.*, in press (2006).

The following papers have also been submitted for journal publication:

- J.C. Mauro and A.K. Varshneya, “*Ab Initio* Modeling of Rigidity Percolation and Incipient Plasticity in Ge-Se Glasses,” *J. Non-Cryst. Solids*, submitted (2006).
- J.C. Mauro and A.K. Varshneya, “Multiscale Modeling of Arsenic Selenide Glass,” *J. Non-Cryst. Solids*, submitted (2006).
- J.C. Mauro, R.J. Loucks, J. Balakrishnan, and A.K. Varshneya, “Mapping the Potential Energy Landscapes of Selenium Clusters,” *J. Non-Cryst. Solids*, submitted (2006).
- J.C. Mauro, R.J. Loucks, J. Balakrishnan, and A.K. Varshneya, “*Ab Initio* Modeling of Volume-Temperature Curves for Glassforming Systems,” *J. Non-Cryst. Solids*, submitted (2006).

The work in this thesis has also been the subject of a number of presentations:

- J.C. Mauro, “Thermodynamic Models of the Glass Transition,” Presented to the CES 585 (Glass Transition Range Behavior) Class at Alfred University, Apr. 6, 2005.
- J.C. Mauro, “Inherent Structures, Inverse Melting, and Kauzmann Curves,” Presented to the CES 585 (Glass Transition Range Behavior) Class at Alfred University, Apr. 18, 2005.
- J.C. Mauro, “Modeling and Simulation at Corning Incorporated,” Presented at the Undergraduate Engineering Seminar at Alfred University, Apr. 28, 2005.
- J.C. Mauro and A.K. Varshneya, “*Ab Initio* Modeling of Glasses in the Sulfur-Selenium System,” 6th Pacific Rim Conference on Ceramic and Glass Technology, PACRIM-GOM-62-2005, Sep. 16, 2005.
- J.C. Mauro, “Multiscale Modeling of Chalcogenides,” Multiscale Materials Modeling Research Group, Massachusetts Institute of Technology, Nov. 4, 2005.
- J.C. Mauro, “Multiscale Modeling of Chalcogenides,” Center for Materials Research, Cornell University, Nov. 14, 2005.

- J.C. Mauro and A.K. Varshneya, “*Ab Initio* Modeling of Chalcogenide Glass Structures,” XV Symposium on Non-Oxide and New Optical Glasses, Bangalore, India, Apr. 10, 2006.
- J.C. Mauro, R.J. Loucks, J. Balakrishnan, and A.K. Varshneya, “Nonequilibrium Statistical Mechanical Model of Structural Relaxation in Glass,” XV Symposium on Non-Oxide and New Optical Glasses, Bangalore, India, Apr. 10, 2006.
- J.C. Mauro, R.J. Loucks, J. Balakrishnan, and A.K. Varshneya, “Mapping the Potential Energy Landscapes of Chalcogen Systems,” XV Symposium on Non-Oxide and New Optical Glasses, Bangalore, India, Apr. 10, 2006.

1.2 Computational Quantum Mechanics

Our multiscale modeling begins at the quantum mechanical level, where we are concerned with solving the Schrödinger equation for a large system of electrons and nuclei. In this chapter, we introduce the Schrödinger equation and discuss the construction of wavefunctions for a many-body system. The many-body Schrödinger equation is not generally soluble by analytical means, so we must turn to numerical simulations in order to compute the energy of realistic molecular systems.

Numerical solutions of the Schrödinger equation rely on the variational principle, which involves construction of a trial wavefunction with a number of adjustable parameters. Minimization of system energy with respect to these parameters can provide a good estimate of the true ground state energy of a system.

The many-body problem is simplified through use of the Born-Oppenheimer approximation, which separates electronic motion from that of the much slower nuclei. Hartree-Fock theory further simplifies the problem by assuming that the electrons see each other as an average field. This allows for the introduction of a single-electron Fock operator, which, when coupled with the variational principle, allows for efficient solution of the Schrödinger

equation for large molecular systems.

The accuracy of the Hartree-Fock result can be improved through use of Rayleigh-Schrödinger perturbation theory. Specifically, the Møller-Plesset technique uses the Rayleigh-Schrödinger formalism to correct for the true electron-electron interactions in a molecular system. In this thesis, we make use of second- and fourth-order Møller-Plesset perturbation theory to derive *ab initio* potentials for chalcogenide systems.

This chapter assumes a basic familiarity with the postulates of quantum mechanics and with Dirac notation. The interested reader is encouraged to review any of several excellent textbooks¹⁻⁴ for an introduction to these concepts. The many-body problem itself is treated more thoroughly by a number of authors.⁵⁻⁹

1.3 The Schrödinger Equation

The quantum mechanical state of a system can be determined by solving the Schrödinger equation. Using Dirac notation, we write

$$\hat{H} |\Psi\rangle = E |\Psi\rangle, \quad (1.1)$$

where $\hat{H}$ is the Hamiltonian operator for the system. The eigenket $|\Psi\rangle$ represents a quantum state of the system with energy eigenvalue E . Since $\hat{H}$ is Hermitian, $|\Psi\rangle$ can be written as a linear combination of eigenkets,

$$|\Psi\rangle = \sum_i c_i |\Phi_i\rangle, \quad (1.2)$$

where the various $|\Phi_i\rangle$ form a complete set and are normalized such that

$$\langle \Phi_j | \Phi_i \rangle = \delta_{ij}. \quad (1.3)$$

The probability amplitude c_j can be found by multiplying both sides of Equation (1.2) by the bra $\langle \Phi_j |$,

$$\langle \Phi_j | \Psi \rangle = \sum_i c_i \langle \Phi_j | \Phi_i \rangle = c_j. \quad (1.4)$$

In a similar fashion, the eigenket $|\Psi\rangle$ can be related to the wavefunction $\Psi(\mathbf{r})$ by

$$\langle \mathbf{r} | \Psi \rangle = \Psi(\mathbf{r}), \quad (1.5)$$

since $\Psi(\mathbf{r})$ is simply a probability amplitude in $\mathbf{r}$ -space.

1.4 Identical Particles

All particles in nature can be classified as either bosons or fermions, where bosons have an integer spin ($s = 0, 1, 2, \dots$) and fermions have a half-integer spin ($s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$). Consider a system of two identical particles with overlapping wavefunctions Ψ_a and Ψ_b . In quantum mechanics, these particles are indistinguishable. Bosons, such as photons and gluons, obey a symmetric wavefunction,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\Psi_a(\mathbf{r}_1) \Psi_b(\mathbf{r}_2) + \Psi_b(\mathbf{r}_1) \Psi_a(\mathbf{r}_2)], \quad (1.6)$$

where the positions of the particles, $\mathbf{r}_1$ and $\mathbf{r}_2$, can be exchanged without altering the composite wavefunction of the system, $\Psi(\mathbf{r}_1, \mathbf{r}_2)$. Fermions, such as protons, neutrons, and electrons, obey an antisymmetric wavefunction,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\Psi_a(\mathbf{r}_1) \Psi_b(\mathbf{r}_2) - \Psi_b(\mathbf{r}_1) \Psi_a(\mathbf{r}_2)], \quad (1.7)$$

where exchange of the particle positions results in negating the wavefunction:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1). \quad (1.8)$$

It follows that two identical fermions cannot occupy the same state, since in this case the wavefunction itself vanishes:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\Psi_a(\mathbf{r}_1) \Psi_a(\mathbf{r}_2) - \Psi_a(\mathbf{r}_1) \Psi_a(\mathbf{r}_2)] = 0. \quad (1.9)$$

This is the famous Pauli exclusion principle.

In this thesis, we are concerned with solving the Schrödinger equation for a many-body fermionic system. An antisymmetric wavefunction for an N -fermion system can be

constructed using a Slater determinant,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(\mathbf{r}_1) & \Psi_2(\mathbf{r}_1) & \Psi_3(\mathbf{r}_1) & \cdots & \Psi_N(\mathbf{r}_1) \\ \Psi_1(\mathbf{r}_2) & \Psi_2(\mathbf{r}_2) & \Psi_3(\mathbf{r}_2) & \cdots & \Psi_N(\mathbf{r}_2) \\ \Psi_1(\mathbf{r}_3) & \Psi_2(\mathbf{r}_3) & \Psi_3(\mathbf{r}_3) & \cdots & \Psi_N(\mathbf{r}_3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Psi_1(\mathbf{r}_N) & \Psi_2(\mathbf{r}_N) & \Psi_3(\mathbf{r}_N) & \cdots & \Psi_N(\mathbf{r}_N) \end{vmatrix}. \quad (1.10)$$

Interchanging the coordinates of any two fermions corresponds to interchanging two rows of the Slater determinant. This changes the sign of the determinant and hence ensures the antisymmetry of the wavefunction. Having two fermions occupying the same state corresponds to having two equal columns in the Slater determinant, which makes the entire determinant zero.

1.5 The Variational Principle

The variational method is a technique for estimating the ground state energy of any system by guessing a trial eigenket $|\Psi_v\rangle$. The trial eigenket can be written as a linear combination of the correct eigenkets,

$$|\Psi_v\rangle = \sum_i c_i |\Psi_i\rangle, \quad (1.11)$$

such that

$$\hat{H} |\Psi_v\rangle = \sum_i c_i E_i |\Psi_i\rangle. \quad (1.12)$$

Multiplying by the bra

$$\langle \Psi_v | = \sum_i c_i^* \langle \Psi_i |, \quad (1.13)$$

we obtain

$$\langle \Psi_v | \hat{H} | \Psi_v \rangle = \sum_j c_j^* \langle \Psi_j | \sum_i c_i E_i | \Psi_i \rangle, \quad (1.14)$$

or

$$\langle \Psi_v | \hat{H} | \Psi_v \rangle = \sum_j \sum_i c_j^* c_i E_i \langle \Psi_j | \Psi_i \rangle. \quad (1.15)$$

This reduces to

$$\langle \Psi_v | \hat{H} | \Psi_v \rangle = \sum_j \sum_i c_j^* c_i E_i \delta_{ij} = \sum_i |c_i|^2 E_i, \quad (1.16)$$

which can be expanded as

$$\langle \Psi_v | \hat{H} | \Psi_v \rangle = |c_0|^2 E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \dots. \quad (1.17)$$

Since the ground state energy is lower than each of the excited state energies ($E_0 < E_1 < E_2 < \dots$), we know that

$$\langle \Psi_v | \hat{H} | \Psi_v \rangle \geq |c_0|^2 E_0 + |c_1|^2 E_0 + |c_2|^2 E_0 + \dots, \quad (1.18)$$

Since $\langle \Psi_v | \Psi_v \rangle = 1$, this simplifies to

$$\langle \Psi_v | \hat{H} | \Psi_v \rangle \geq E_0. \quad (1.19)$$

Equation (1.19) is known as the variational principle. Although its derivation is

very simple, the implications are quite profound. Any trial eigenket $|\Psi_v\rangle$ that is chosen will yield an energy no less than the actual ground state energy E_0 of the system. Thus, a variational solution to the Schrödinger equation can be found by choosing a form for $|\Psi_v\rangle$ with a number of adjustable parameters. These parameters can then be optimized by minimizing $\langle\Psi_v|\hat{H}|\Psi_v\rangle$. If a realistic form of $|\Psi_v\rangle$ is chosen (such as a linear combination of atomic orbitals for a molecular system), the minimum value of $\langle\Psi_v|\hat{H}|\Psi_v\rangle$ will represent a good approximation to the actual ground state energy E_0 . This is an extremely powerful technique for solving for the ground state of any quantum mechanical system.

1.6 The Born-Oppenheimer Approximation

The most fundamental approximation made in many-body quantum theory is the Born-Oppenheimer approximation, which separates the Hamiltonian of the fast-moving electrons from that of the slower-moving nuclei such that the electrons are considered to move in a field of fixed nuclei. The general Hamiltonian for a molecular system is

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}, \quad (1.20)$$

where

$$\hat{T}_e = \sum_i \frac{\hat{p}_i^2}{2m} \quad (1.21)$$

is the kinetic energy of the electrons and

$$\hat{T}_N = \sum_n \frac{\hat{p}_n^2}{2M_n} \quad (1.22)$$

is the kinetic energy of the nuclei. The repulsive electron-electron Coulomb potential is denoted $\hat{V}_{ee}$, the attractive electron-nucleus interaction is $\hat{V}_{eN}$, and the repulsive nucleus-nucleus interaction is $\hat{V}_{NN}$. The electrons and nuclei have masses of m and M_n , respectively, and $\hat{p}$ is the momentum operator.

The Born-Oppenheimer approximation takes advantage of the fact that $M_n \gg m$, such that the kinetic energy of the nuclei is much less than that of the electrons. This allows us to write two separate Hamiltonian which act on different time scales:

$$\hat{H}_{elec} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN}, \quad (1.23)$$

and

$$\hat{H}_{nuc} = \hat{T}_N + \hat{V}_{NN}. \quad (1.24)$$

The solution of the electronic Schrödinger equation,

$$\hat{H}_{elec} |\Psi_{elec}\rangle = E_{elec} |\Psi_{elec}\rangle, \quad (1.25)$$

is the electronic eigenstate,

$$|\Psi_{elec}\rangle = |\Psi_{elec}(\{\mathbf{r}_i\}; \{\mathbf{R}_n\})\rangle, \quad (1.26)$$

which depends explicitly on the electronic coordinates $\{\mathbf{r}_i\}$ but only parametrically on the nuclear positions $\{\mathbf{R}_n\}$. In other words, for different values of $\{\mathbf{R}_n\}$, $|\Psi_{elec}\rangle$ is a different function of $\{\mathbf{r}_i\}$. After determining $|\Psi_{elec}\rangle$, the repulsive energy of the fixed nuclei must

be included in the final value for the molecular energy:

$$E_{tot} = E_{elec} + \langle \Psi_{nuc} | \hat{V}_{NN} | \Psi_{nuc} \rangle. \quad (1.27)$$

Since the computation of $\langle \Psi_{nuc} | \hat{V}_{NN} | \Psi_{nuc} \rangle$ is trivial, from now on we will only be concerned with solving for the electronic system of Equation (1.25). As such, we will drop the “*elec*” subscripts.

1.7 Hartree-Fock Theory

Even with the Born-Oppenheimer approximation, a solution of the Schrödinger equation for a many-electron system is not readily obtained. Hartree-Fock theory simplifies the problem further by assuming that the electrons see each other as an average field. To derive this theory, let us consider a trial wavefunction Ψ_v , given in the form of a Slater determinant with a number of variational parameters. The expectation value of the Hamiltonian operator $\hat{H}$ is a number given by

$$E[\Psi_v] = \langle \Psi_v | \hat{H} | \Psi_v \rangle, \quad (1.28)$$

where $E[\Psi_v]$ is a functional of Ψ_v . Suppose we vary Ψ_v by an arbitrarily small amount,

$$\Psi_v \rightarrow \Psi_v + \delta\Psi_v. \quad (1.29)$$

The energy then becomes

$$E[\Psi_v + \delta\Psi_v] = \langle \Psi_v + \delta\Psi_v | \hat{H} | \Psi_v + \delta\Psi_v \rangle \quad (1.30)$$

$$= E[\Psi_v] + \langle \delta\Psi_v | \hat{H} | \Psi_v \rangle + \langle \Psi_v | \hat{H} | \delta\Psi_v \rangle + \dots \quad (1.31)$$

$$= E[\Psi_v] + \delta E + \dots, \quad (1.32)$$

where δE is the first variation in E , including all terms that are linear in the variation $\delta\Psi_v$.

According to the variational method, we are looking for the form of Ψ_v where $E[\Psi_v]$ is a minimum. In other words, we want to find the Ψ_v for which $\delta E = 0$. Given a variational trial eigenket,

$$|\Psi_v\rangle = \sum_i c_i |\Psi_i\rangle, \quad (1.33)$$

we wish to minimize the energy

$$E = \langle \Psi_v | \hat{H} | \Psi_v \rangle = \sum_i \sum_j c_i^* c_j \langle \Psi_i | \hat{H} | \Psi_j \rangle \quad (1.34)$$

subject to the constraint that the trial wavefunction remains normalized, i.e.,

$$\langle \Psi_v | \Psi_v \rangle - 1 = \sum_i \sum_j c_i^* c_j \langle \Psi_i | \Psi_j \rangle - 1 = 0. \quad (1.35)$$

Using Lagrange's method of undetermined multipliers, we can minimize the functional

$$\mathcal{L} = \langle \Psi_v | \hat{H} | \Psi_v \rangle - \mathcal{E} (\langle \Psi_v | \Psi_v \rangle - 1) \quad (1.36)$$

$$= \sum_i \sum_j c_i^* c_j \langle \Psi_i | \hat{H} | \Psi_j \rangle - \mathcal{E} \sum_i \sum_j (c_i^* c_j \langle \Psi_i | \Psi_j \rangle - 1), \quad (1.37)$$

where $\mathcal{E}$ is the Lagrange multiplier. The first variation in $\mathcal{L}$ is

$$\begin{aligned}\delta\mathcal{L} = & \sum_i \sum_j \delta c_i^* c_j \langle \Psi_i | \hat{H} | \Psi_j \rangle - \mathcal{E} \sum_i \sum_j \delta c_i^* c_j \langle \Psi_i | \Psi_j \rangle + \\ & \sum_i \sum_j c_i^* \delta c_j \langle \Psi_i | \hat{H} | \Psi_j \rangle - \mathcal{E} \sum_i \sum_j c_i^* \delta c_j \langle \Psi_i | \Psi_j \rangle = 0.\end{aligned}\quad (1.38)$$

After collecting terms and interchanging indices, we obtain

$$\sum_i \delta c_i^* \sum_j (H_{ij} c_j - \mathcal{E} S_{ij} c_j) + c.c. = 0, \quad (1.39)$$

where $H_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle$. The linear expansion functions $|\Psi_i\rangle$ are not assumed to be orthogonal, but rather overlap according to

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle. \quad (1.40)$$

Since δc_i^* is arbitrary, we must have

$$\sum_i \sum_j (H_{ij} c_j - \mathcal{E} S_{ij} c_j) = 0. \quad (1.41)$$

This can be rewritten in matrix notation as

$$\mathbf{H}\mathbf{c} = \mathcal{E}\mathbf{S}\mathbf{c}, \quad (1.42)$$

where $\mathbf{H}$ and $\mathbf{S}$ are matrices containing the elements of H_{ij} and S_{ij} , respectively, and $\mathbf{c}$ is a column vector of the c_j values.

The Hamiltonian itself can be written as

$$\hat{H} = \sum_i \hat{h}_i + \frac{1}{2} \sum_i \sum_{j \neq i} \hat{g}_{ij}, \quad (1.43)$$

where $\hat{h}_i$ contains the single-electron energy terms,

$$\hat{h}_i = -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_n \frac{Z_n q_e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_n|}, \quad (1.44)$$

and $\hat{g}_{ij}$ is the electron-electron interaction,

$$\hat{g}_{ij} = \frac{q_e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}. \quad (1.45)$$

The first term in Equation (1.44) is the kinetic energy of the electron. The second term accounts for the electron-nuclear interaction potential, where the summation is over all nuclei in the system. The position of the n^{th} nucleus is $\mathbf{R}_n$, and its atomic number is Z_n ; q_e is the elementary charge, and ϵ_0 is the permittivity of free space.

In order to simplify the many-body problem, we introduce an effective single-electron operator, $\hat{f}_i$, called the Fock operator:

$$\hat{f}_i = -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_n \frac{Z_n q_e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_n|} + \hat{v}_i^{HF}. \quad (1.46)$$

The Fock operator is the sum of the core Hamiltonian operator $\hat{h}_i$ and an effective one-electron potential operator, $\hat{v}_i^{HF}$, called the Hartree-Fock potential. The Hartree-Fock potential is the average potential experienced by an electron due to the presence of the

other electrons. It is defined as

$$\hat{v}_i^{HF} = \hat{J}_i - \hat{K}_i, \quad (1.47)$$

where $\hat{J}_i$ is the Coulomb operator,

$$\hat{J}_i = \frac{q_e^2}{4\pi\epsilon_0} \sum_j \int d^3\mathbf{r}_j \Psi_j^* r_{ij}^{-1} \Psi_j, \quad (1.48)$$

and $\hat{K}_i$ is the exchange operator,

$$\hat{K}_i = \frac{q_e^2}{4\pi\epsilon_0} \sum_j \int d^3\mathbf{r}_j \Psi_j^* r_{ij}^{-1} \Psi_i. \quad (1.49)$$

In terms of these operators, we can write the energy of the system as

$$E^{HF} = \sum_i \left\langle \Psi_i \left| \hat{h}_i + \frac{1}{2} (\hat{J}_i - \hat{K}_i) \right| \Psi_i \right\rangle. \quad (1.50)$$

As we shall see in the next two sections, the Hartree-Fock energy E^{HF} can be corrected for the true electron-electron interactions using perturbation theory.

1.8 Rayleigh-Schrödinger Perturbation Theory

Suppose that we have solved the Schrödinger equation,

$$\hat{H}_0 \left| \Psi_i^{(0)} \right\rangle = E_i^{(0)} \left| \Psi_i^{(0)} \right\rangle, \quad (1.51)$$

for some Hamiltonian $\hat{H}_0$ and now wish to perturb the system with a new interaction Hamiltonian $\hat{H}_I$. In other words, we wish to solve the new eigenvalue problem,

$$\hat{H} |\Psi_i\rangle = \left(\hat{H}_0 + \hat{H}_I \right) |\Psi_i\rangle = E_i |\Psi_i\rangle, \quad (1.52)$$

where the eigenkets and eigenvalues of $\hat{H}_0$ have already been determined. Rayleigh-Schrödinger perturbation theory is a systematic procedure for obtaining approximate solutions to the above perturbed problem by building on the known solutions of the unperturbed case. This is done by introducing an order parameter λ , which is later set to unity, and writing

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_I. \quad (1.53)$$

The exact eigenvalues of Equation (1.52) can be expanded in a Taylor series in λ ,

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots \quad (1.54)$$

Similarly, the eigenkets can be written as

$$|\Psi_i\rangle = |\Psi_i^{(0)}\rangle + \lambda |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle + \dots \quad (1.55)$$

Substituting these expanded forms into Equation (1.52), we obtain

$$\begin{aligned} & \left(\hat{H}_0 + \lambda \hat{H}_I \right) \left(|\Psi_i^{(0)}\rangle + \lambda |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle + \dots \right) \\ &= \left(E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots \right) \left(|\Psi_i^{(0)}\rangle + \lambda |\Psi_i^{(1)}\rangle + \lambda^2 |\Psi_i^{(2)}\rangle + \dots \right). \end{aligned} \quad (1.56)$$

Collecting the zeroth-order λ^0 terms, we obtain the unperturbed eigenvalue problem

$$\hat{H}_0 \left| \Psi_i^{(0)} \right\rangle = E_i^{(0)} \left| \Psi_i^{(0)} \right\rangle, \quad (1.57)$$

which has already been solved. The corrections to $E_i^{(0)}$ and $\left| \Psi_i^{(0)} \right\rangle$ are found by considering the higher powers of λ .

Equating the coefficients of λ^1 , we obtain the first-order perturbation equation

$$\left(\hat{H}_0 - E_i^{(0)} \right) \left| \Psi_i^{(1)} \right\rangle = \left(E_i^{(1)} - \hat{H}_I \right) \left| \Psi_i^{(0)} \right\rangle. \quad (1.58)$$

The first-order correction to the energy, $E_i^{(1)}$, can be found by multiplying both sides of the equation by the unperturbed bra $\left\langle \Psi_i^{(0)} \right|$, such that

$$E_i^{(1)} = \left\langle \Psi_i^{(0)} \right| \hat{H}_I \left| \Psi_i^{(0)} \right\rangle. \quad (1.59)$$

In other words, the first-order correction to the energy is simply the expectation value of the perturbation in the unperturbed state.

The first-order correction to the eigenstate can be found by noting that the various $\left| \Psi_i^{(0)} \right\rangle$ eigenstates form a complete set. Taking $\left| \Psi_i^{(n)} \right\rangle$ ($n = 0, 1, 2, \dots$) to be mutually orthogonal, we write

$$\left| \Psi_j^{(1)} \right\rangle = \sum_{i \neq j} c_i \left| \Psi_i^{(0)} \right\rangle. \quad (1.60)$$

Substituting into Equation (1.58), we have

$$\left(\hat{H}_0 - E_j^{(0)}\right) \sum_{i \neq j} c_i \left| \Psi_i^{(0)} \right\rangle = \left(E_j^{(1)} - \hat{H}_I\right) \left| \Psi_j^{(0)} \right\rangle, \quad (1.61)$$

or

$$\sum_{i \neq j} c_i \left(E_i^{(0)} - E_j^{(0)}\right) \left| \Psi_i^{(0)} \right\rangle = \left(E_j^{(1)} - \hat{H}_I\right) \left| \Psi_j^{(0)} \right\rangle. \quad (1.62)$$

Multiplying by $\left\langle \Psi_k^{(0)} \right|$,

$$\sum_{i \neq j} c_i \left(E_i^{(0)} - E_j^{(0)}\right) \left\langle \Psi_k^{(0)} \right| \Psi_i^{(0)} \rangle = E_j^{(1)} \left\langle \Psi_k^{(0)} \right| \Psi_j^{(0)} \rangle - \left\langle \Psi_k^{(0)} \right| \hat{H}_I \left| \Psi_j^{(0)} \right\rangle, \quad (1.63)$$

which reduces to

$$\sum_{i \neq j} c_i \left(E_i^{(0)} - E_j^{(0)}\right) \delta_{ik} = E_j^{(1)} \delta_{jk} - \left\langle \Psi_k^{(0)} \right| \hat{H}_I \left| \Psi_j^{(0)} \right\rangle. \quad (1.64)$$

Since $j \neq k$, we have

$$c_k \left(E_k^{(0)} - E_j^{(0)}\right) = - \left\langle \Psi_k^{(0)} \right| \hat{H}_I \left| \Psi_j^{(0)} \right\rangle, \quad (1.65)$$

and

$$c_k = \frac{\left\langle \Psi_k^{(0)} \right| \hat{H}_I \left| \Psi_j^{(0)} \right\rangle}{E_j^{(0)} - E_k^{(0)}}. \quad (1.66)$$

Substituting into Equation (1.58), we obtain the first-order correction to the eigenstate,

$$\left| \Psi_j^{(1)} \right\rangle = \sum_{i \neq j} \frac{\left\langle \Psi_i^{(0)} \right| \hat{H}_I \left| \Psi_j^{(0)} \right\rangle}{E_j^{(0)} - E_i^{(0)}} \left| \Psi_i^{(0)} \right\rangle. \quad (1.67)$$

Hence, the energy eigenvalues and eigenkets according to first-order perturbation theory are

$$E_i \approx E_i^{(0)} + \left\langle \Psi_i^{(0)} \left| \hat{H}_I \right| \Psi_i^{(0)} \right\rangle \quad (1.68)$$

and

$$|\Psi_i\rangle \approx |\Psi_i^{(0)}\rangle + \sum_{i \neq j} \frac{\left\langle \Psi_i^{(0)} \left| \hat{H}_I \right| \Psi_j^{(0)} \right\rangle}{E_j^{(0)} - E_i^{(0)}} |\Psi_j^{(0)}\rangle, \quad (1.69)$$

respectively.

A more accurate approximation can be obtained by considering second- and higher-order corrections. Equating the λ^2 coefficients of Equation (1.56) and multiplying by $\left\langle \Psi_i^{(0)} \right|$, we obtain

$$E_i^{(2)} = \left\langle \Psi_i^{(0)} \left| \hat{H}_I \right| \Psi_i^{(1)} \right\rangle. \quad (1.70)$$

Substituting Equation (1.67) into the above expression, we have

$$E_j^{(2)} = \left\langle \Psi_j^{(0)} \left| \hat{H}_I \sum_{i \neq j} \frac{\left\langle \Psi_i^{(0)} \left| \hat{H}_I \right| \Psi_j^{(0)} \right\rangle}{E_j^{(0)} - E_i^{(0)}} \right| \Psi_i^{(0)} \right\rangle, \quad (1.71)$$

which simplifies to

$$E_j^{(2)} = \sum_{i \neq j} \frac{\left| \left\langle \Psi_i^{(0)} \left| \hat{H}_I \right| \Psi_j^{(0)} \right\rangle \right|^2}{E_j^{(0)} - E_i^{(0)}}. \quad (1.72)$$

Higher order corrections can be computed in a similar fashion.

1.9 Møller-Plesset Perturbation Theory

Møller-Plesset perturbation theory is a particular implementation of the Rayleigh-Schrödinger formalism that seeks to improve the Hartree-Fock estimate of energy by ac-

counting for the true electron correlation energy via a perturbation expansion.¹⁰ The Hamiltonian is partitioned as

$$\hat{H} = \hat{H}_0 + \hat{H}_I, \quad (1.73)$$

where $\hat{H}_0$ is the Hartree-Fock Hamiltonian, given by the summation of Fock operators:

$$\hat{H}_0 = \sum_i \hat{f}_i = \sum_i \left(\hat{h}_i + \hat{J}_i - \hat{K}_i \right). \quad (1.74)$$

Note that the Hartree-Fock energy, E^{HF} from Equation (1.50), is *not* the expectation value of the Hartree-Fock Hamiltonian. Rather, $\hat{H}_0$ is an approximate Hamiltonian for which the Hartree-Fock ground state $|\Psi^{(0)}\rangle$ is an exact eigenfunction, satisfying

$$\hat{H}_0 |\Psi^{(0)}\rangle = E^{(0)} |\Psi^{(0)}\rangle, \quad (1.75)$$

where

$$E^{(0)} = \sum_i \left\langle \Psi_i^{(0)} \left| \hat{f}_i \right| \Psi_i^{(0)} \right\rangle = \sum_i \varepsilon_i \quad (1.76)$$

is just the zeroth-order perturbation energy. According to Møller-Plesset perturbation theory, the perturbing Hamiltonian $\hat{H}_I$ is chosen to be the difference between the actual electron-electron correlation energy and the average potential assumed by Hartree-Fock:

$$\hat{H}_I = \frac{q_e^2}{4\pi\epsilon_0} \sum_i \sum_{j<i} \frac{1}{r_{ij}} - \sum_i \hat{v}_i^{HF} \quad (1.77)$$

$$= \frac{q_e^2}{4\pi\epsilon_0} \sum_i \sum_{j<i} \frac{1}{r_{ij}} - \sum_i \left(\hat{J}_i - \hat{K}_i \right). \quad (1.78)$$

With this definition of $\hat{H}_I$, the first-order perturbation energy is

$$E^{(1)} = \langle \Psi^{(0)} | \hat{H}_I | \Psi^{(0)} \rangle \quad (1.79)$$

$$= \frac{q_e^2}{4\pi\epsilon_0} \sum_i \sum_{j < i} \langle \Psi_i^{(0)} | \frac{1}{r_{ij}} | \Psi_j^{(0)} \rangle - \sum_i \langle \Psi_i^{(0)} | \hat{J}_i - \hat{K}_i | \Psi_i^{(0)} \rangle \quad (1.80)$$

$$= -\frac{1}{2} \sum_i \langle \Psi^{(0)} | \hat{J}_i - \hat{K}_i | \Psi^{(0)} \rangle. \quad (1.81)$$

Therefore, the Hartree-Fock energy E^{HF} is recovered from the first-order perturbation in Møller-Plesset theory:

$$E^{HF} = E^{(0)} + E^{(1)} \quad (1.82)$$

$$= \sum_i \langle \Psi_i^{(0)} | \hat{f}_i | \Psi_i^{(0)} \rangle - \frac{1}{2} \sum_i \langle \Psi^{(0)} | \hat{J}_i - \hat{K}_i | \Psi^{(0)} \rangle, \quad (1.83)$$

which simplifies to

$$E^{HF} = \sum_i \langle \Psi_i^{(0)} | \hat{h}_i + \hat{J}_i - \hat{K}_i | \Psi_i^{(0)} \rangle - \frac{1}{2} \sum_i \langle \Psi^{(0)} | \hat{J}_i - \hat{K}_i | \Psi^{(0)} \rangle \quad (1.84)$$

$$= \sum_i \langle \Psi_i^{(0)} | \hat{h}_i + \frac{1}{2} (\hat{J}_i - \hat{K}_i) | \Psi_i^{(0)} \rangle. \quad (1.85)$$

Thus, the first correction to the Hartree-Fock energy occurs in the second-order of the perturbation expansion,

$$E^{(2)} = \sum_i \frac{|\langle \Psi_i^{(0)} | \hat{H}_I | \Psi^{(0)} \rangle|^2}{E^{(0)} - E_i^{(0)}}. \quad (1.86)$$

Implementations of Møller-Plesset perturbation theory generally use up to fourth-order corrections. The level of theory is typically denoted by MP n , where n is the highest-

order used in the perturbation expansion. In this thesis, we make use of MP2 and MP4 levels of theory.

Chapter 2

Model Interatomic Potentials

Accurate descriptions of interatomic potentials are necessary to model and understand the structure and properties of materials. Ideally, these potentials are developed using a first principles approach, which is most likely to accurately describe the interatomic forces. For larger atoms, however, this approach has proved difficult. As a result, researchers often use empirical or semi-empirical models to describe the effective behavior of the atomic systems without necessarily capturing all of the true underlying physics.

The pioneering work of Stillinger, Weber, and LaViolette¹¹ was the first successful attempt at describing the interatomic potentials of sulfur. Using experimental structural data and a trial-and-error process, Stillinger and coworkers developed expressions for both two- and three-atom interactions in liquid sulfur. Application of these potentials in a molecular dynamics simulation successfully reproduced the short-range order found in liquid sulfur at different temperatures. In addition, Rustad, Yuen, and Spera¹² used the Stillinger model and nonequilibrium molecular dynamics to investigate the behavior of liquid sulfur

under extreme shear. Another empirical model of sulfur was developed by Kastowky and Bradaczek¹³ and used to calculate the structure of sulfur molecules.

Oligschleger *et al.*¹⁴ developed model potentials for selenium following an approach similar to Stillinger and coworkers in their model of sulfur. Combining experimental data with density functional calculations, Oligschleger *et al.* developed effective two- and three-body interaction potentials that reproduce known structures and energies of selenium clusters (Se₂-Se₈). The Oligschleger model of selenium has been used to determine selenium glass structure,¹⁵ vibrational properties,¹⁶ and quench behavior.¹⁷⁻¹⁹ While both the Stillinger and Oligschleger models have enabled much progress in the study of sulfur and selenium, they are not based on fundamental physics and hence are inherently limited in scope and applicability.

This problem may be addressed using quantum mechanical techniques. Descôte and Bichara²⁰ employed a semi-empirical quantum mechanical technique to study the structure of liquid sulfur, but their model relies on knowing much of this structural data *a priori*. Thus, this model cannot be used to predict new structures beyond what has already been measured experimentally.

Shimojo *et al.*²¹⁻²³ investigated the structure and electrical properties of fluid selenium using density functional theory (DFT), a quantum mechanical technique pioneered by Hohenberg and Kohn²⁴ that relates the total electronic energy to the electron density. Zhang and Drabold^{25,26} utilized additional localization techniques by Sankey and Niklewski²⁷ to study the impact of photon absorption on the structure of amorphous selenium. In addition, Shimizu *et al.*²⁸ and Nakamura and Ikawa²⁹ performed molecular

orbital calculations on amorphous selenium and found excellent agreement between their calculated structures and those determined by infrared/Raman spectrometry. However, none of this work at the quantum mechanical level has attempted to bridge the gap to larger scale molecular dynamics or Monte Carlo simulations.

There has been very little work in the modeling of elemental tellurium, and none of it has been particularly successful. Attempts at modeling tellurium with density functional theory have produced highly incorrect results,³⁰ such as predicting a coordination number of six for liquid tellurium instead of the correct value of two. There have been no previous modeling efforts in the heterogeneous Se-Te system. The only previous theoretical investigation of the heterogeneous S-Se system is a DFT study of the ground states of small S-Se clusters.³¹

Previous modeling of elemental arsenic includes molecular orbital^{32,33} and DFT³⁴ studies of small As clusters. Density functional theory has also been used to study the structure of liquid arsenic^{35,36} and liquid As₂S₃, As₂Se₃, and As₂Te₃.³⁷

Semi-empirical models of germanium, including two- and three-body terms, have previously been used to study elemental clusters, liquids, crystals, and the amorphous state.³⁸⁻⁴⁰ Subsequent DFT studies have investigated liquid Ge⁴¹ and GeSe.⁴² Liquid and glassy GeSe₂ have been studied with DFT by a number of researchers.⁴³⁻⁴⁸ There have been no previous modeling efforts in the Ge-As-Se system.

In this chapter, we use *ab initio* molecular modeling and a cluster expansion technique to derive effective interaction potentials for elemental sulfur, selenium, tellurium, arsenic, and germanium. We also develop *ab initio* potentials for the binary S-Se, Se-Te,

As-Se, Ge-Se, and Ge-As systems and the ternary Ge-As-Se system. We will use these potentials in classical Monte Carlo simulations to investigate the structure of chalcogenide glasses.

2.1 Choice of Basis Set

Any molecular orbital calculation requires specification of an appropriate basis set, i.e., a linear combination of mathematical functions from which the wavefunction is constructed. For computational convenience, basis sets are typically constructed from a set of primitive Gaussian functions. In order to accurately describe the molecular orbitals of a system, it is often necessary to use a large basis set composed of tens or even hundreds of primitive Gaussians.

In our modeling of sulfur, selenium, arsenic, and germanium, we use the aug-cc-pVQZ basis sets of Dunning and coworkers,^{49,50} where the acronym stands for “augmented correlation-consistent polarized valence quadruple- ζ .” As a “quadruple- ζ ” basis set, each orbital is represented by four basis functions, and the term “augmented” implies that additional diffuse functions are used to represent non-localized electrons; these diffuse functions are especially important for large atoms like selenium. “Polarized valence” refers to the presence of additional basis functions at the valence to increase mathematical flexibility. Finally, “correlation-consistent” implies that the basis set has been optimized for calculations including electron correlations, such as in Møller-Plesset perturbation theory. The aug-cc-pVQZ basis set allows for explicit representation of all electrons in every atom of the simulation. For selenium, the aug-cc-pVQZ basis set uses 93 basis functions composed of

343 primitive Gaussians.

This explicit representation of electrons does not scale well to very large atoms such as tellurium, which has 52 electrons per atom. In this case, we employ a small-core relativistic pseudopotential⁵¹ in which the inner shell electrons are combined with the nucleus as an effective core. For tellurium, the $n = 1, 2, 3$ shells are incorporated into the effective core, and the $4s^2p^6d^{10}5s^2p^4$ outer electrons are modeled explicitly. The corresponding basis set is denoted aug-cc-pVQZ-pp and contains 27 basis functions with 87 primitive Gaussians.

Unfortunately, we found that a combination of the aug-cc-pVQZ basis set for selenium with the aug-cc-pVQZ-pp basis set for tellurium in heterogeneous systems did not lead to well-converged energy values due to excessive mixing of frozen core and valence orbitals between atoms. In order to address this problem, we use aug-cc-pVQZ-pp basis sets for both tellurium and selenium in all heterogeneous Se-Te simulations. The aug-cc-pVQZ-pp basis set for selenium incorporates the $n = 1, 2$ shells into an effective core and models explicitly the $3s^2p^6d^{10}4s^2p^4$ outer electrons.

The total potentials of individual atoms using the MP2 and MP4 levels of theory are shown in Table I in units of hartrees, where $1 \text{ hartree} = 27.211 \text{ eV} = 627.51 \text{ kcal/mol} = 2626 \text{ kJ/mol}$. We use the Gaussian 03 software⁵² for all quantum-level simulations. The pseudopotential basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database.⁵³

Table I. Total Potential Energy of a Single Atom (units of hartrees)

Level of Theory	MP2	MP4	MP4
Basis Set	aug-cc-pVQZ	aug-cc-pVQZ	aug-cc-pVQZ-pp
Sulfur	−397.6409303	−397.6665769	N/A
Selenium	−2400.106568	−2400.124998	−2373.527355
Tellurium	N/A	N/A	−6547.122362
Arsenic	−2234.443255	−2234.457287	N/A
Germanium	−2075.550212	−2075.564534	N/A

2.2 Cluster Expansion Theory

In order to calculate multi-body interaction potentials, we adopt the technique of cluster expansion.^{54,55} Cluster expansion assumes that the total potential of a system is the sum of the single-atom energies and all combinations of higher-order interactions. Mathematically, we can write the total potential as

$$U = \sum_{i=1}^N U_{1,i} + \sum_{i=1}^N \sum_{j \neq i}^N U_{2,ij}(r_{ij}) + \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq i,j}^N U_{3,ijk}(r_{ij}, r_{jk}, \theta_{ijk}) + \cdots, \quad (2.1)$$

where U_n refers to the n^{th} -order interaction potential. In theory, the series of interactions terminates only with the U_N term, where N is the total number of atoms in the system. However, since the magnitudes of the interactions typically decrease with increasing n (and due to computational efficiency considerations), it is common to truncate the series after the second- or third-order terms.

The U_1 term contributes by far the most energy to the system, often several orders of magnitude larger than all other terms combined. For a simulation with constant number of atoms, the contribution of the total system energy from U_1 will remain constant. As a

result, for closed systems we are concerned only with modeling the *interaction* potentials between atoms, i.e., U_n where $n > 1$; the U_1 term itself can be neglected in these simulations. However, in cluster expansion theory, accurate computation of U_1 is still necessary in order to isolate the many-body effects. Since U_1 is so much larger than the interaction potentials, U_1 must be computed with as much precision as possible.

For each order of interaction, it is necessary to determine the generalized coordinates that affect the energy of the system. For U_1 there are no degrees of freedom since any translation of the monomer yields the same one-body potential. For U_2 there is one degree of freedom, r_{ij} , the two-body separation distance. For the U_3 term we consider three generalized coordinates: two separation distances, r_{ij} and r_{jk} , and the subtended angle, θ_{ijk} . (Alternatively, we could consider three separation distances, r_{ij} , r_{jk} , and r_{ik} , but it is usually more intuitive and convenient to express V_3 in terms of a bond angle.) The number of generalized coordinates increases dramatically with increased order of interaction.

In order to compute an n^{th} -order interaction potential as a function of its generalized coordinates, we first simulate systems of 1, 2, 3, $\dots$, $(n-1)$ particles to determine all lower-order interactions. Then, the total potential of n -atom systems should be calculated using different coordinates in phase space. Finally, the n^{th} -order interaction can be isolated by subtracting all lower-order contributions:

$$\begin{aligned} \sum \sum \cdots \sum U_n(\cdots) &= U(\cdots) - \sum_{i=1}^N U_1 - \sum_{i=1}^N \sum_{j \neq i}^N U_2(r_{ij}) - \cdots \\ &\quad - \sum \sum \cdots \sum U_{n-1}(\cdots). \end{aligned} \tag{2.2}$$

For example, after the one-body potentials have been computed, the two-body interaction

can be calculated from the total dimer potential as

$$\sum_{i=1}^2 \sum_{j \neq i}^2 U_{2,ij}(r_{ij}) = U(r_{ij}) - \sum_{i=1}^2 U_{1,i}. \quad (2.3)$$

Accounting for symmetry and assuming an elemental system, this simplifies to

$$2U_2(r_{ij}) = U(r_{ij}) - 2U_1. \quad (2.4)$$

The same technique can then be applied to three-body and all higher order interactions.

2.3 Two-Body Interaction Potentials

In order to be used in higher-level classical simulations (e.g., molecular dynamics and Monte Carlo), the *ab initio* potentials are fit to continuous functions that accurately reproduce the quantum data. We compute the potential energy of two-body clusters as a function of interatomic separation distance, r_{ij} , using the MP4 level of theory. Following cluster expansion theory, the two-body interaction potential is calculated by subtracting the potentials of the isolated monomers from the total dimer potential:

$$2U_{2,ij}(r_{ij}) = U(r_{ij}) - \sum_{i=1}^2 U_{1,i}. \quad (2.5)$$

The two-body interaction potential for the homogeneous S-S, Se-Se, Te-Te, As-As, and Ge-Ge dimers are plotted in Figure 2.1, and potentials for the heterogeneous dimers are given in Figure 2.2.

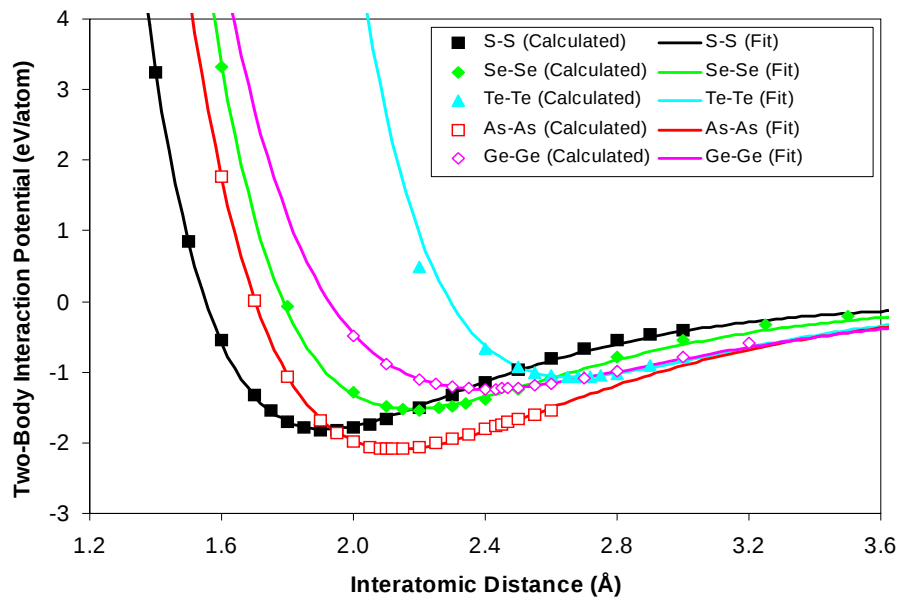


Figure 2.1. Two-body interaction potentials for elemental sulfur, selenium, tellurium, arsenic, and germanium.

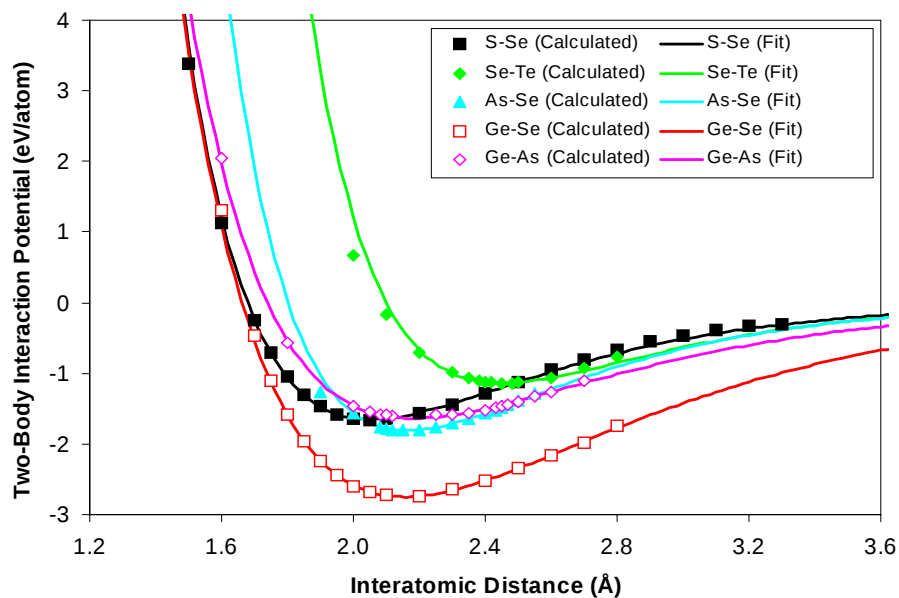


Figure 2.2. Two-body interaction potentials for heteropolar dimers.

Table II. Parameters for the Homogeneous Two-Body Interaction Potentials

	S-S	Se-Se	Te-Te	As-As	Ge-Ge
D_0 (eV)	1.80499785	1.517550	1.070009	2.092012	1.239626
r_0 (Å)	1.91298491	2.173489	2.667650	2.132471	2.399151
α (Å ⁻¹)	1.91906871	1.790250	1.852509	1.609369	1.465028

We fit the *ab initio* data using a Morse potential⁵⁶ of the form

$$U_2(r_{ij}) = D_0 e^{-2\alpha(r_{ij}-r_0)} - 2D_0 e^{-\alpha(r_{ij}-r_0)} \quad (2.6)$$

$$= D_0 \left[\left(1 - e^{-\alpha(r_{ij}-r_0)} \right)^2 - 1 \right], \quad (2.7)$$

where D_0 is the potential well depth, r_0 is the equilibrium separation distance, and α is the shape parameter. Using a least-squares fitting routine, we determine optimized values of D_0 , r_0 , and α for all interaction pairs. These values are provided in Tables II and III for homogeneous and heterogeneous pairs of atoms, respectively.

Note that the *total* two-body interaction potential for a given dimer is

$$U_2(r_{ij}) + U_2(r_{ji}) = 2U_2(r_{ij}). \quad (2.8)$$

For example, the total cohesive energy of the Se-Se dimer is $2D_0 = 3.0351$ eV. Given a system of N atoms, the total two-body interaction potential for the ensemble is

$$U_{2,tot} = \sum_{i=1}^N \sum_{j \neq i}^N U_{2,ij}(r_{ij}) = 2 \sum_{i=1}^N \sum_{j>i}^N U_{2,ij}(r_{ij}). \quad (2.9)$$

Table III. Parameters for the Heterogeneous Two-Body Interaction Potentials

	S-Se	Se-Te	As-Se	Ge-Se	Ge-As
D_0 (eV)	1.6524751	1.135962	1.808382	2.751080	1.637631
r_0 (Å)	2.0520452	2.449647	2.162598	2.155640	2.183368
α (Å ⁻¹)	1.8585684	1.981215	1.921385	1.405003	1.559512

2.4 Three-Body Interaction Potentials

In order to calculate three-body interaction potentials, we compute the total potential energies of the various trimers of interest using the MP2 level of theory. (MP4 is too computationally intensive for the three-body systems.) The three-body interaction is isolated by subtracting the one- and two-body contributions:

$$U_{3,ijk}(r_{ij}, r_{jk}, \theta_{ijk}) = U(r_{ij}, r_{jk}, \theta_{ijk}) - \sum_{i=1}^3 U_{1,i} - 2 \sum_{i=1}^3 \sum_{j>i}^3 U_{2,ij}(r_{ij}), \quad (2.10)$$

where r_{ij} is the separation distance between atoms i and j , r_{jk} is the separation between atoms j and k , and θ_{ijk} is the bond angle. Simulations are performed for fixed values of $r_{ij} = r_{jk}$ and varying bond angle θ_{ijk} . Following the examples of Stillinger¹¹ and Oligschleger,¹⁴ we fit the three-body interaction potentials using a separable function,

$$U_{3,ijk}(r_{ij}, r_{jk}, \theta_{ijk}) = R_{ij}(r_{ij}) R_{jk}(r_{jk}) \Theta_{ijk}(\theta_{ijk}). \quad (2.11)$$

For the radial components, $R_{ij}(r_{ij})$ and $R_{jk}(r_{jk})$, we adopt the form

$$R(r) = b \operatorname{sech}(cr), \quad (2.12)$$

where b and c are constants. Note that for an elemental cluster such as Se-Se-Se, $R(r) = R_{ij}(r) = R_{jk}(r)$; in a heterogeneous cluster the radial functions are defined separately for each pairwise combination of elements.

Due to symmetry reasons the angular component, $\Theta_{ijk}(\theta_{ijk})$, of the three-body potential must be an even function, so we assume a Fourier cosine solution,

$$\Theta(\theta) = \frac{1}{2}a_0 + \sum_{m=1}^M a_m \cos(m\theta). \quad (2.13)$$

We determine the constants in the above equations by fitting the *ab initio* data using a least-square error routine. Extra weight is given to fitting the *ab initio* data at higher bond angles, since two-body interactions dominate at low angles. We truncate the Fourier series in Equation (2.13) with $M = 18$ in order to provide a good fit of important features in the *ab initio* data.

Optimized parameters for the radial components are shown in Tables IV and V for elemental and heterogeneous trimers, respectively. The Fourier coefficients for the angular components are provided in Tables VI through XII.

Fitting is performed first on the elemental trimers, shown in Figure 2.3. While two-body terms are dominant at low angles, care is taken that the three-body interactions extrapolate to some positive energy at $\theta = 0$. Low-angle extrapolations for the elemental trimers are shown in Figure 2.4. Next, we perform fitting for the binary sulfur-selenium trimers, S-Se-S, S-S-Se, Se-S-Se, and S-Se-Se, shown in Figure 2.5. We take the values of $b_{\text{S-S,Se-Se}}$ and $c_{\text{S-S,Se-Se}}$ from our previous fits of the elemental S-S-S and Se-Se-Se trimers. Figure 2.6 shows extrapolation of these fits to low bond angles. This fitting procedure is

repeated for the remaining binary systems, with results shown in Figures 2.7 through 2.16.

Finally, results for the ternary Ge-As-Se system are shown in Figures 2.15 and 2.16.

Note that in our formulation the total three-body interaction potential for any three atoms, i , j , and k , is the sum of all permutations:

$$\begin{aligned}
U_{3,tot} = & R_{ij}(r_{ij}) R_{jk}(r_{jk}) \Theta_{ijk}(\theta_{ijk}) + R_{ji}(r_{ji}) R_{ik}(r_{ik}) \Theta_{jik}(\theta_{jik}) + \\
& R_{ik}(r_{ik}) R_{kj}(r_{kj}) \Theta_{ikj}(\theta_{ikj}) + R_{ki}(r_{ki}) R_{ij}(r_{ij}) \Theta_{kij}(\theta_{kij}) + \\
& R_{jk}(r_{jk}) R_{ki}(r_{ki}) \Theta_{jki}(\theta_{jki}) + R_{kj}(r_{kj}) R_{ji}(r_{ji}) \Theta_{kji}(\theta_{kji}). \quad (2.14)
\end{aligned}$$

Taking into account symmetry considerations, the expression simplifies to

$$\begin{aligned}
U_{3,tot} = & 2R_{ij}(r_{ij}) R_{jk}(r_{jk}) \Theta(\theta_{ijk}) + 2R_{ij}(r_{ij}) R_{ik}(r_{ik}) \Theta(\theta_{kij}) + \\
& 2R_{ik}(r_{ik}) R_{jk}(r_{jk}) \Theta(\theta_{jki}). \quad (2.15)
\end{aligned}$$

Thus the total three-body interaction potential for the entire system is

$$U_{3,tot} = 2 \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq i, k > j}^N U_{3,ijk}(r_{ij}, r_{jk}, \theta_{ijk}). \quad (2.16)$$

The total interaction energies of the various trimers can be determined by summing the two- and three-body interaction potentials. Figure 2.17 shows this total multi-body interaction potential as a function of bond angle for the S-S-S, Se-Se-Se, and Te-Te-Te clusters assuming equilibrium bond lengths for r_{ij} and r_{jk} . Whereas the minimum energy configurations for the S-S-S and Se-Se-Se trimers are at a bond angles of 115-120°, the

minimum energy configuration for Te-Te-Te occurs with a bond angle of 65° . The Te-Te-Te cluster has a second (relative) minimum around 110° , and the S-S-S and Se-Se-Se clusters have a second minimum at around 65° . This “dual minimum” behavior is in good agreement with experimental cluster measurements for sulfur,^{57,58} selenium,¹⁴ and tellurium,⁵⁹ which predict two distinct optimized geometries: an open triangular structure and a closed, equilateral triangle.

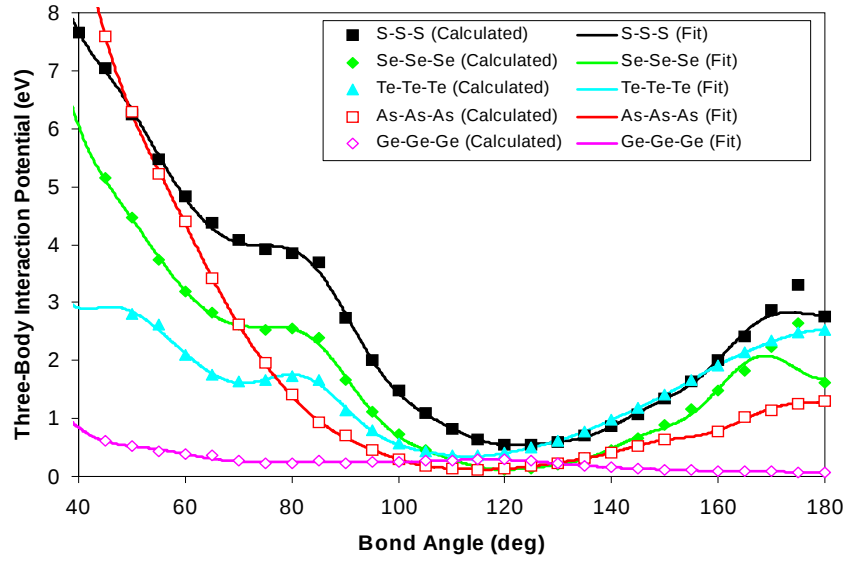


Figure 2.3. Three-body interaction potentials for elemental sulfur, selenium, tellurium, arsenic, and germanium at $r_{ij} = r_{jk} = r_0$ for each pair of elements.

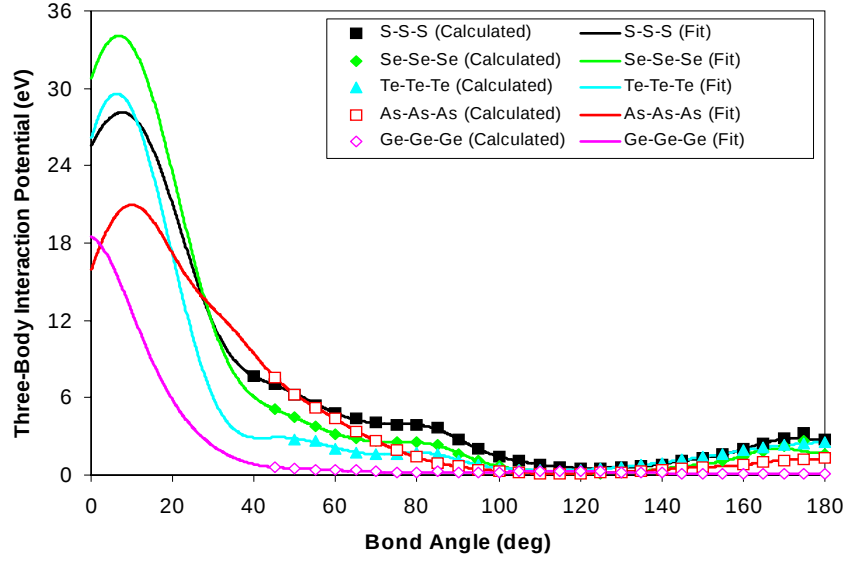


Figure 2.4. Extrapolated three-body interaction potentials for the elemental trimers.

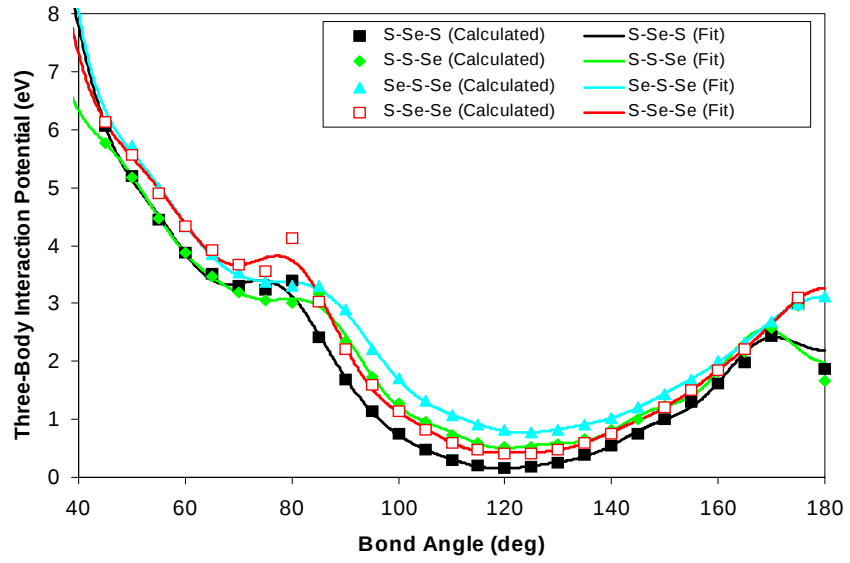


Figure 2.5. Three-body interaction potentials for the binary sulfur-selenium system at $r_{ij} = r_{jk} = 2.0527 \text{ \AA}$.

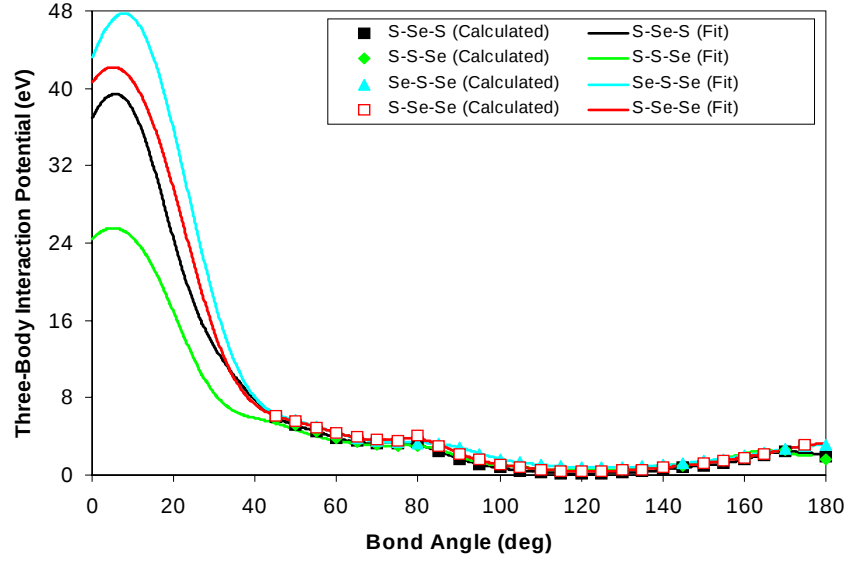


Figure 2.6. Extrapolated three-body interaction potentials for the binary S-Se system.

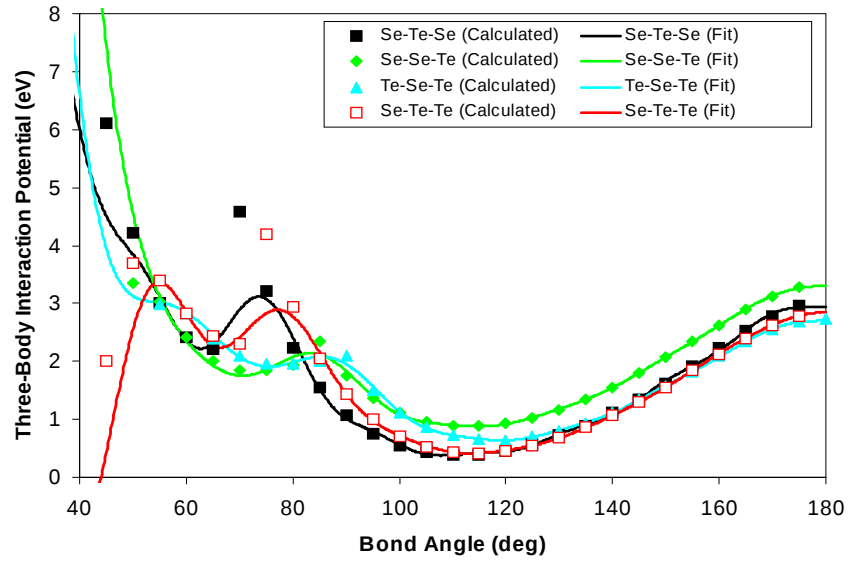


Figure 2.7. Three-body interaction potentials for the binary selenium-tellurium system at $r_{ij} = r_{jk} = 2.4496 \text{ \AA}$.

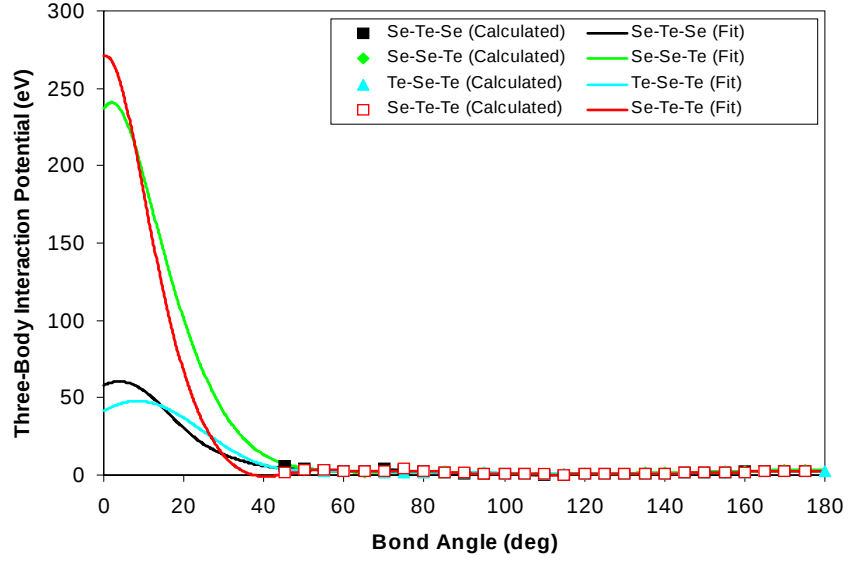


Figure 2.8. Extrapolated three-body interaction potentials for the binary Se-Te system.

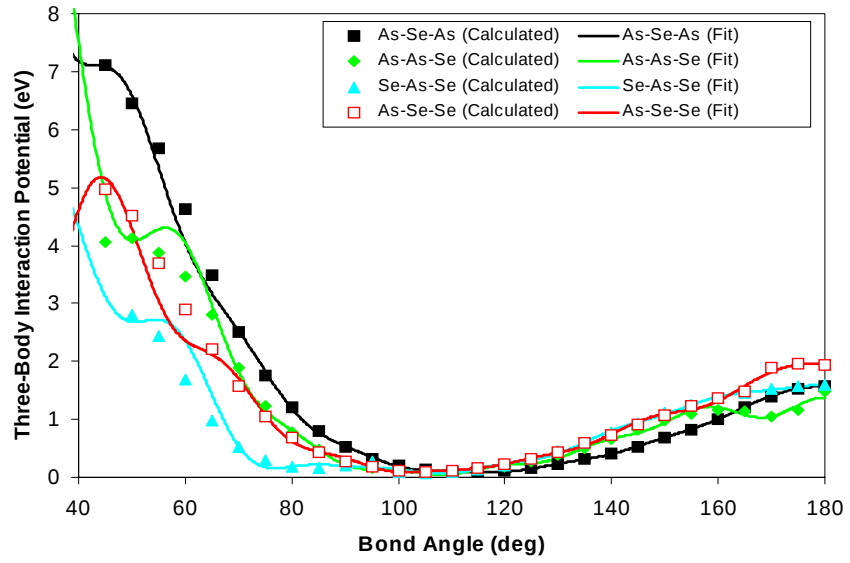


Figure 2.9. Three-body interaction potentials for the binary arsenic-selenium system at $r_{ij} = r_{jk} = 2.5 \text{ \AA}$.

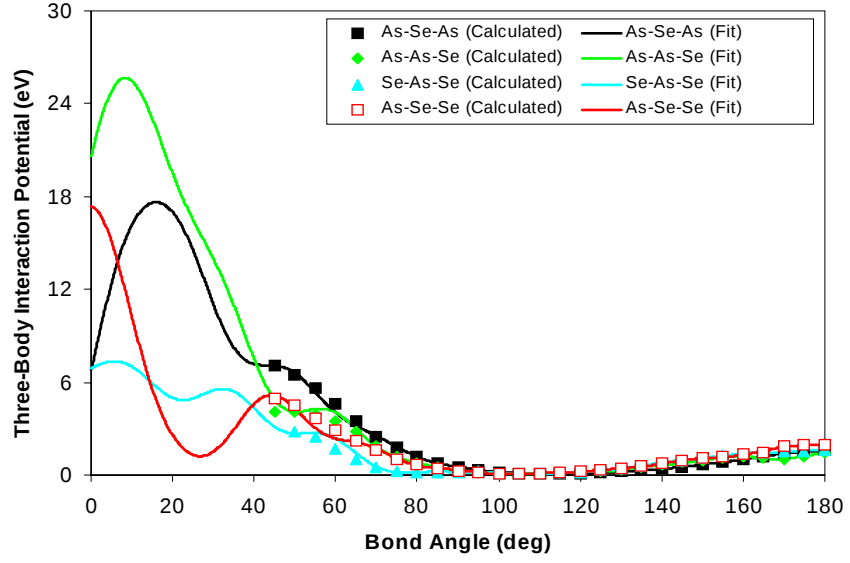


Figure 2.10. Extrapolated three-body interaction potentials for the binary As-Se system.

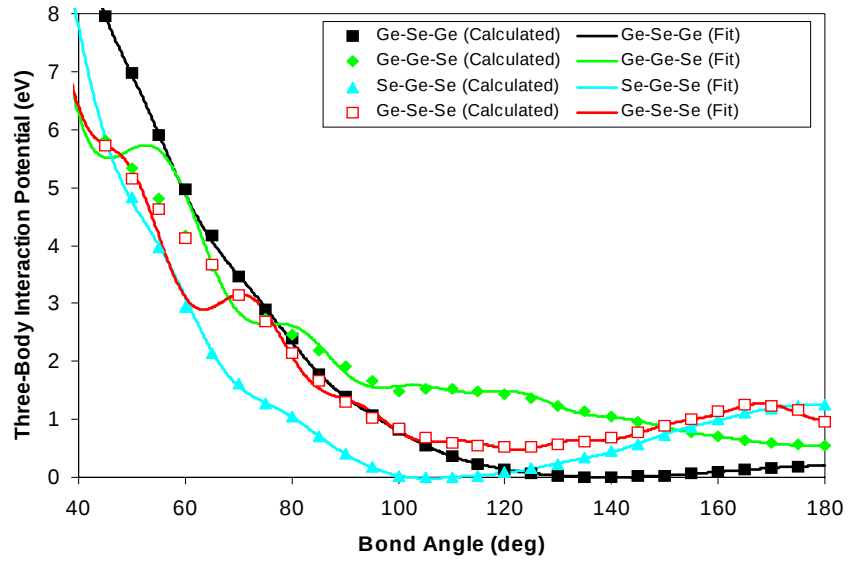


Figure 2.11. Three-body interaction potentials for the binary germanium-selenium system at $r_{ij} = r_{jk} = 2.5 \text{ \AA}$.

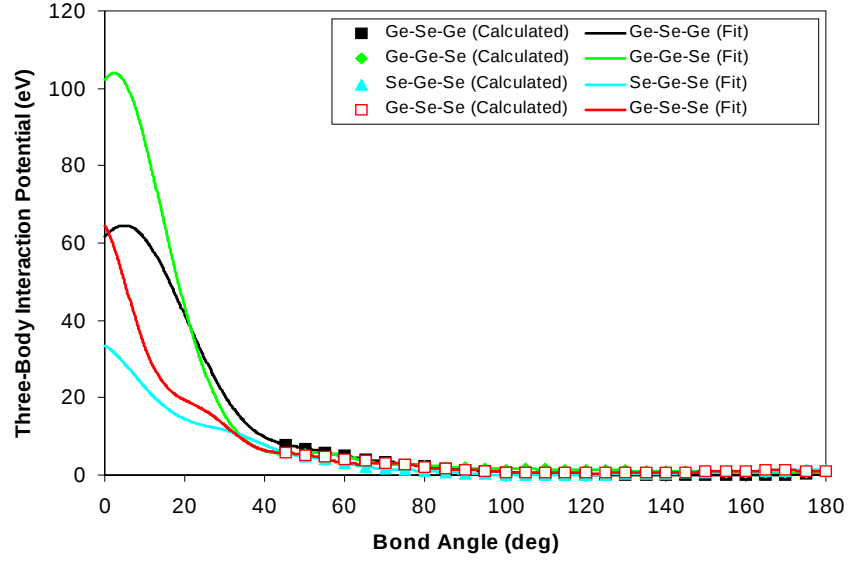


Figure 2.12. Extrapolated three-body interaction potentials for the binary Ge-Se system.

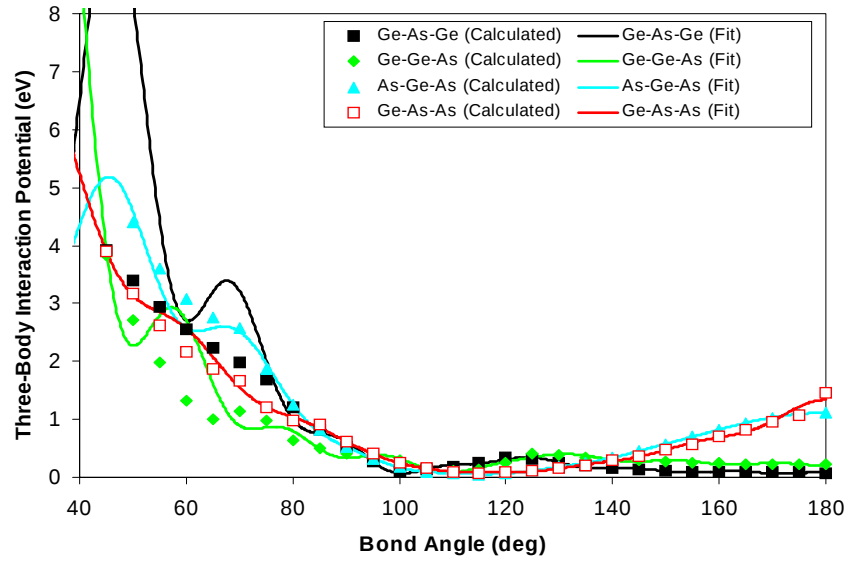


Figure 2.13. Three-body interaction potentials for the binary germanium-arsenic system at $r_{ij} = r_{jk} = 2.5 \text{ \AA}$.

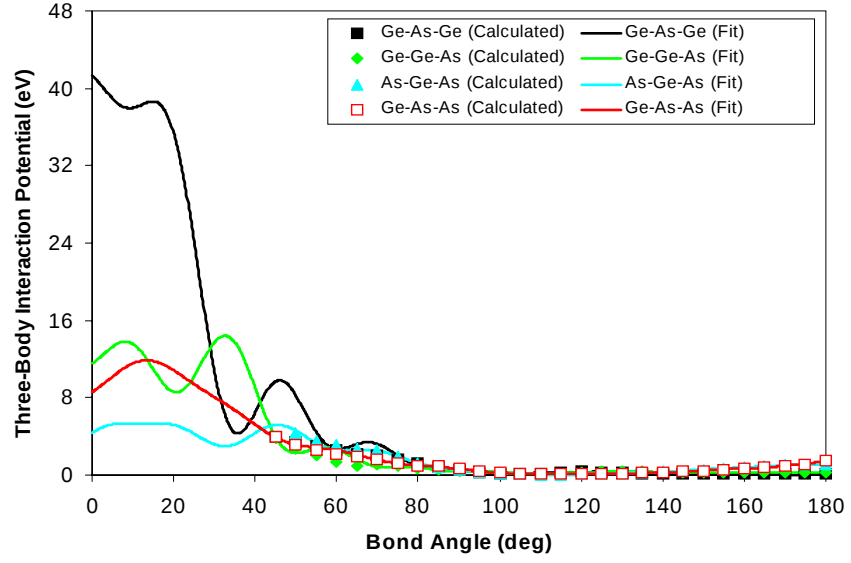


Figure 2.14. Extrapolated three-body interaction potentials for the binary Ge-As system.

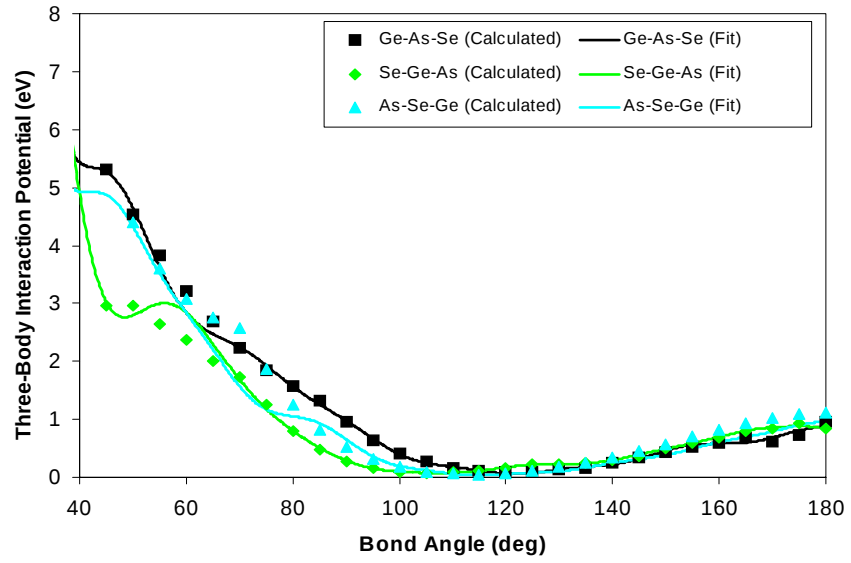


Figure 2.15. Three-body interaction potentials for the ternary germanium-arsenic-selenium system at $r_{ij} = r_{jk} = 2.5 \text{ \AA}$.

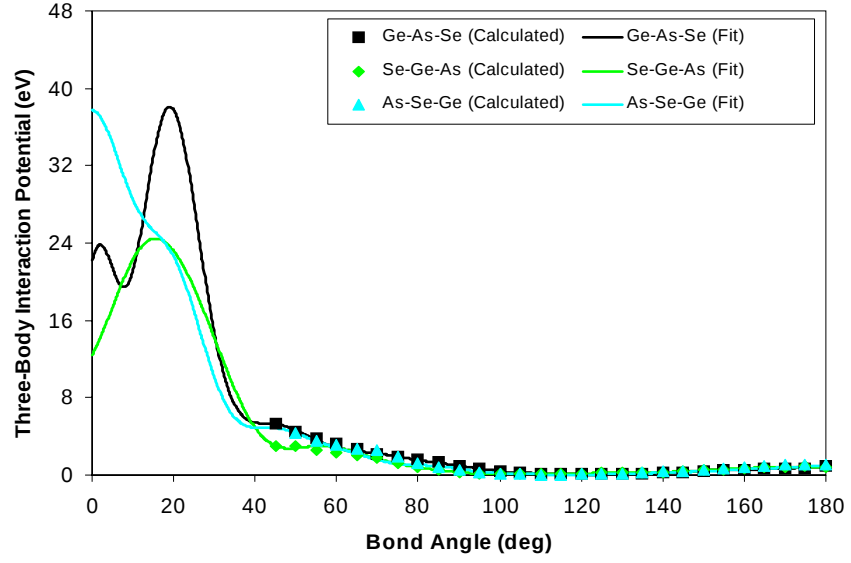


Figure 2.16. Extrapolated three-body interaction potentials for the ternary Ge-As-Se system.

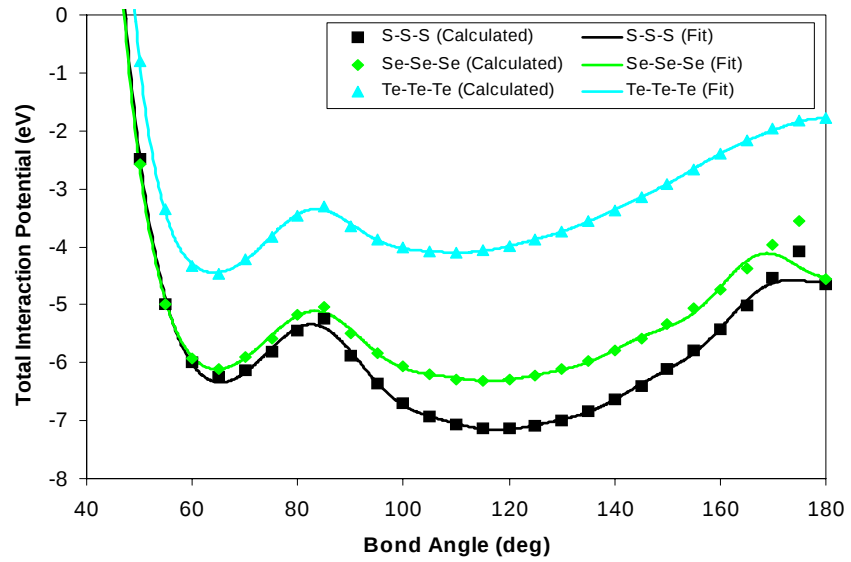


Figure 2.17. Total two- plus three-body interaction potentials for the S-S-S, Se-Se-Se, and Te-Te-Te trimers at $r_{ij} = r_{jk} = r_0$.

Table IV. Homogeneous Two-Body Radial Parameters for the Three-Body Interaction Potentials

	S-S	Se-Se	Te-Te	As-As	Ge-Ge
b (eV ^{1/2})	4.4643122	7.9074605	6.1277354	0.310383	0.992756
c (Å ⁻¹)	1.4089831	1.4510428	1.3972349	1.727836	1.500000

Table V. Heterogeneous Two-Body Radial Parameters for the Three-Body Interaction Potentials

	S-Se	Se-Te	As-Se	Ge-Se	Ge-As
b (eV ^{1/2})	6.2119469	19.076068	0.407885	6.938291	0.214437
c (Å ⁻¹)	1.3515589	2.1406499	1.581859	2.000798	1.068536

Table VI. Three-Body Fourier Coefficients for the Elemental Trimers

	S-S-S	Se-Se-Se	Te-Te-Te	As-As-As	Ge-Ge-Ge
a_0	2.5209085	1.4737009	6.3815150	5963.0799	351.914690
a_1	-2.3800373	-0.7488205	-7.2938000	-1308.3017	29.206466
a_2	-1.2322490	-0.3235095	-0.8722934	-737.2801	-23.110155
a_3	-1.8707962	-0.8336347	-5.3866029	-5702.1420	76.585262
a_4	0.0661656	0.3661849	-1.1660934	-1917.9391	3.310100
a_5	-0.2388731	0.0559816	-1.4283849	-88.2395	-20.881477
a_6	0.1311631	0.0506636	-0.2498004	1250.3015	7.628035
a_7	0.0489161	-0.0042692	0.2152772	657.1982	1.903190
a_8	0.1809061	-0.0116419	0.6061612	966.7898	0.564988
a_9	-0.0022569	-0.0636407	-0.0489911	576.2556	1.655172
a_{10}	-0.3279935	-0.3031730	-1.0056510	636.6168	-11.158179
a_{11}	-0.3907347	-0.2478697	-1.2943361	212.9018	-4.505804
a_{12}	-0.2596401	-0.2017648	-0.6955193	-70.9160	11.911857
a_{13}	-0.0391134	0.0186467	-0.0892812	-521.6409	12.593301
a_{14}	-0.0600140	-0.0517747	0.0788748	-788.6293	8.505400
a_{15}	0.0002528	0.0337409	0.0481918	-724.8093	3.272179
a_{16}	-0.0125521	-0.0149274	0.1699672	-691.4643	-3.029141
a_{17}	0.0605235	0.0537881	0.2387772	-352.5857	-3.103025
a_{18}	-0.0028334	-0.0063938	0.1788512	-222.3367	-1.270753

Table VII. Three-Body Fourier Coefficients for the Heterogeneous S-Se-S, S-S-Se, Se-S-Se, and S-Se-Se Trimers

	S-Se-S	S-S-Se	Se-S-Se	S-Se-Se
a_0	1.2183252	2.8555385	2.0356276	1.4239221
a_1	-0.4938253	-0.7805802	-1.1444016	-1.1947322
a_2	0.1253943	-0.5052337	-0.7839961	-0.6643760
a_3	-0.3868286	-1.0397844	-0.6272820	-0.6861257
a_4	0.5232214	0.4608983	0.5837225	0.6597807
a_5	0.1191132	0.0507676	0.0615490	0.1995165
a_6	0.1643227	0.0841439	0.1139735	0.2146434
a_7	0.0065064	-0.0088773	-0.0085916	-0.0423155
a_8	0.0425734	0.0004760	0.0027530	0.0181715
a_9	0.0824306	-0.1904425	-0.2062313	-0.1346219
a_{10}	-0.0287008	-0.5398316	-0.2880510	-0.2286437
a_{11}	-0.0929698	-0.4169818	-0.2500148	-0.3096873
a_{12}	-0.1323757	-0.3025326	-0.0690876	-0.1347800
a_{13}	-0.0366498	-0.0043958	-0.0002147	-0.0010731
a_{14}	-0.1064618	-0.0863026	0.0150516	0.0524841
a_{15}	-0.0993453	0.0793184	0.0043558	-0.0022850
a_{16}	-0.1611172	0.0195371	0.0197465	0.0042689
a_{17}	-0.0675304	0.1258474	0.0036008	0.0267898
a_{18}	-0.0519736	-0.0297712	-0.0106217	0.0413820

Table VIII. Three-Body Fourier Coefficients for the Heterogeneous Se-Te-Se, Se-Se-Te, Te-Se-Te, and Se-Te-Te Trimers

	Se-Te-Se	Se-Se-Te	Te-Se-Te	Se-Te-Te
a_0	19.264535	9.1619754	22.223224	7.2979673
a_1	-17.273420	-10.1123940	-13.462698	-10.259955
a_2	-2.4874198	-2.6299683	5.2217488	-5.0139178
a_3	-11.597780	-5.2549641	0.5202633	-8.6622940
a_4	1.3381763	0.7451214	4.7205673	-0.2471748
a_5	-0.0107653	0.0009848	-5.6671392	0.2233760
a_6	-0.0344267	0.0509585	-2.3424787	0.5589294
a_7	-1.7371929	0.2655886	2.7865778	0.2058917
a_8	0.3212924	0.7741911	2.9739254	-0.0053356
a_9	2.0171056	-0.1361319	-0.5264682	-1.6691366
a_{10}	1.2612500	-1.1315190	-1.7323615	-3.3067562
a_{11}	-1.2352494	-1.1231347	0.0921489	-3.3001658
a_{12}	-2.3823570	-0.3718989	1.9353049	-1.2803732
a_{13}	-1.2790921	0.0757642	1.7476688	0.9489806
a_{14}	-0.1052132	0.0033640	0.5419944	1.6485507
a_{15}	-0.4400456	-0.0269044	0.0828253	0.8962156
a_{16}	-1.9463542	0.1257210	0.0224998	0.0075327
a_{17}	-2.2185852	0.2181182	-0.0360265	-0.2410890
a_{18}	-1.4913421	0.0463594	-0.2454533	-0.0602311

Table IX. Three-Body Fourier Coefficients for the Heterogeneous As-Se-As, As-As-Se, Se-As-Se, and As-Se-Se Trimers

	As-Se-As	As-As-Se	Se-As-Se	As-Se-Se
a_0	3221.485	4743.6116	3493.1265	9.8512234
a_1	505.22827	102.90211	-749.42661	-103.40046
a_2	745.56917	1415.2321	-230.15066	-0.017185972
a_3	-1007.0001	-1717.1846	-1329.9301	-5.0192143
a_4	-0.60141828	-161.44122	-1095.8384	55.397467
a_5	-419.88064	700.88213	-190.77686	70.809932
a_6	-858.45185	151.1445	255.98217	81.006945
a_7	-999.93347	-8.3439707	-28.091459	68.267664
a_8	-408.48981	-352.90103	-685.63583	61.15029
a_9	-138.39041	53.017501	-783.31046	44.712615
a_{10}	0.12182297	827.45096	-436.59039	31.226385
a_{11}	43.205972	1373.6404	0.018804362	10.508458
a_{12}	195.06909	1488.4261	196.32365	0.007131125
a_{13}	387.54611	697.06031	33.472081	-4.774371
a_{14}	547.31548	-7.2535653	-257.28443	-0.015958192
a_{15}	553.25242	-725.81357	-379.4647	9.4038126
a_{16}	393.68351	-567.62639	-318.03461	11.01707
a_{17}	175.04005	-428.95292	-168.6433	9.4174194
a_{18}	13.07628	74.368862	0.001394742	1.9676911

Table X. Three-Body Fourier Coefficients for the Heterogeneous Ge-Se-Ge, Ge-Ge-Se, Se-Ge-Se, and Ge-Se-Se Trimers

	Ge-Se-Ge	Ge-Ge-Se	Se-Ge-Se	Ge-Se-Se
a_0	82.945859	397.584790	82.921031	8.911976
a_1	91.592285	132.869480	-0.236906	-11.805593
a_2	83.105557	0.012418	1.600026	-7.284772
a_3	54.487405	-21.512127	-56.882352	-8.210666
a_4	31.408274	-52.018548	-31.232760	-2.782941
a_5	-4.175893	-27.482655	1.382681	-2.157868
a_6	-14.957023	0.044432	39.773257	-1.525588
a_7	-9.446081	7.847918	53.648097	0.000008
a_8	-1.633654	0.000058	32.720027	0.000060
a_9	0.000001	-13.150164	9.715971	0.000008
a_{10}	-0.721175	-27.179969	-2.089577	-1.311332
a_{11}	-0.384855	-22.033792	-3.213719	-0.961830
a_{12}	2.308721	-0.001137	-0.000024	-0.366157
a_{13}	5.981354	12.099748	0.192213	2.189979
a_{14}	8.280630	8.173760	-3.085069	3.688234
a_{15}	6.972707	-3.900059	-7.034189	4.173368
a_{16}	3.448765	-8.984208	-7.562722	2.144111
a_{17}	0.718317	-0.000191	-5.010979	0.005655
a_{18}	-0.037279	4.192944	-2.427981	-1.075268

Table XI. Three-Body Fourier Coefficients for the Heterogeneous Ge-As-Ge, Ge-Ge-As, As-Ge-As, and Ge-As-As Trimers

	Ge-As-Ge	Ge-Ge-As	As-Ge-As	Ge-As-As
a_0	-3462.1793	1404.8113	1700.2259	-763.53905
a_1	-2663.9909	487.67617	592.72331	-1751.7486
a_2	-1217.9738	-36.244085	-79.718116	0.49346212
a_3	-129.07575	-124.60316	-573.64104	76.769423
a_4	612.06046	-185.37242	-141.80538	1287.4393
a_5	853.18457	-145.46597	-12.895968	782.24732
a_6	302.92659	-3.0496823	-1.5231763	640.34738
a_7	-59.225925	-35.447699	-50.105351	-158.02807
a_8	-40.090299	-0.22664552	1.2403059	-505.95488
a_9	-312.38841	154.42274	36.890344	-572.66263
a_{10}	-695.00043	282.33193	0.1451221	-315.21813
a_{11}	-868.80274	326.10055	-78.738406	-208.97741
a_{12}	-743.4105	232.68569	-112.82708	-49.446725
a_{13}	-375.30926	59.33348	-54.174407	-161.42138
a_{14}	107.86213	-105.02239	58.080641	-201.01169
a_{15}	475.60263	-220.81499	134.97435	-272.39222
a_{16}	547.45189	-235.41696	129.66449	-139.04657
a_{17}	368.01327	-154.2873	70.250843	-79.281276
a_{18}	126.63061	-57.127906	16.125145	4.2465131

Table XII. Three-Body Fourier Coefficients for the Heterogeneous Ge-As-Se, Se-Ge-As, and As-Se-Ge Trimers

	Ge-As-Se	Se-Ge-As	As-Se-Ge
a_0	3437.3228	0.88161965	302.3577
a_1	2026.214	-58.550219	-2.6466402
a_2	1112.9897	60.175349	-55.881024
a_3	217.98378	0.090727669	-201.82237
a_4	462.67885	16.66222	0.9998426
a_5	267.61854	-13.389274	35.581883
a_6	44.81003	-22.14782	38.387415
a_7	-0.71312651	-41.110226	-20.719506
a_8	53.008038	-39.447784	-67.358034
a_9	-14.267328	-12.510683	-80.150916
a_{10}	-135.66139	3.489125	-37.748826
a_{11}	-203.69251	8.6762959	17.198688
a_{12}	-82.408512	1.9688586	51.309807
a_{13}	42.131571	0.002897036	31.242799
a_{14}	176.72105	6.7650875	-9.4914689
a_{15}	173.80961	13.514421	-29.384284
a_{16}	149.82438	11.361956	-14.442467
a_{17}	51.748109	8.5712395	3.1249156
a_{18}	0.87458256	2.3508663	9.6720386

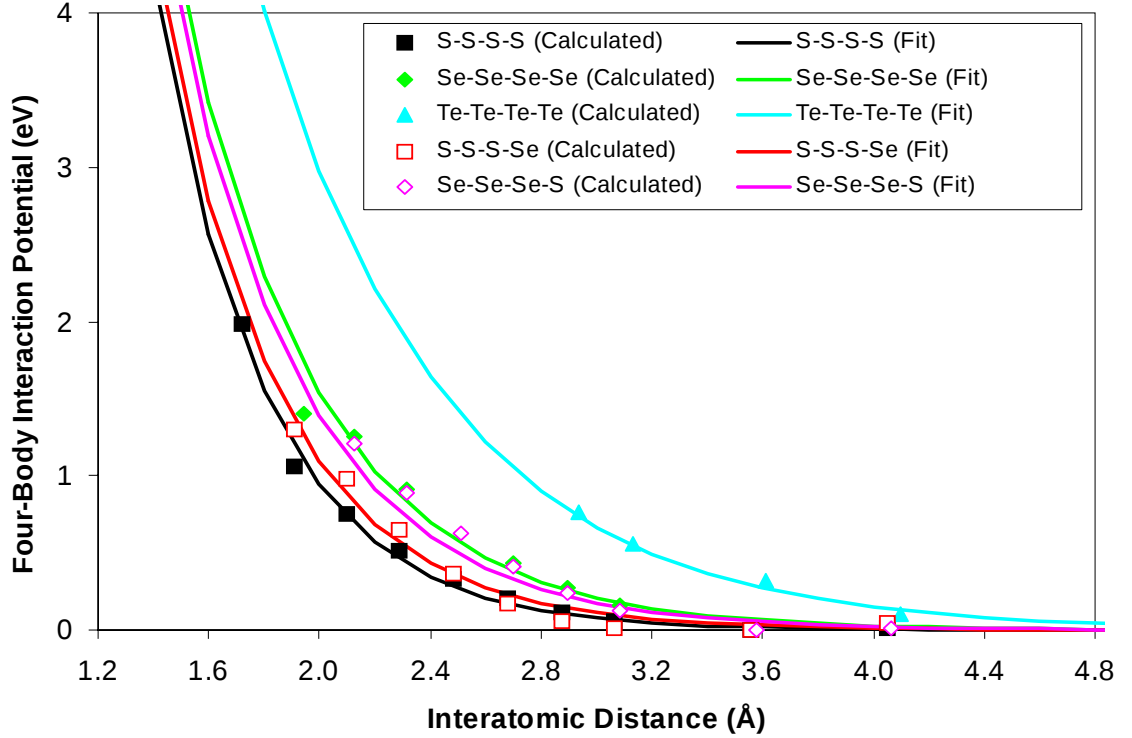


Figure 2.18. Effective four-body potentials.

2.5 Effective Four-Body Interactions

For the case of a four-body cluster we have six generalized coordinates: three interatomic separation distances, r_{ij} , r_{jk} , and r_{kl} ; two bond angles, θ_{ijk} and θ_{jkl} ; and one torsion angle, ϕ_{ijkl} . This six-dimensional phase space is much too large to explore fully at the quantum mechanical level; moreover, a full description of the four-body interaction would lead to computation times in the classical simulation that scale as $O(N^4)$, which is impractical for systems of hundreds or thousands of atoms. Therefore, we model the four-body interaction for the chalcogen systems as an effective pairwise repulsion that depends only on the separation distance between an atom and its third- and longer-distance

Table XIII. Parameters for the Effective Four-Body Interaction Potential

	Sulfur	Selenium	Tellurium
g (eV)	70	42	30
h ($\text{\AA}^{-1}$)	2.5	2.0	1.5

neighbors. Computation of this effective four-body interaction in a classical simulation is on the order of $O(N^2)$, which is small compared to the $O(N^3)$ three-body calculation.

In order to determine this effective repulsion, we introduce a fourth atom to the three-body clusters discussed in the previous section. We assume a bond angle of $\theta_{ijk} = 60^\circ$ and equilibrium bond lengths for the trimers. The fourth atom is positioned equidistant to these three atoms, and the total four-body potential is calculated as a function of this variable separation distance d_l . The four-body interaction is isolated from the two- and three-body contributions using the standard cluster expansion approach:

$$\begin{aligned}
 U_{4,ijkl} = & U(d_l) - \sum_{i=1}^4 U_{1,i} - 2 \sum_{i=1}^4 \sum_{j>i}^4 U_{2,ij}(r_{ij}) - \\
 & 2 \sum_{i=1}^N \sum_{j \neq i}^N \sum_{k \neq i, k > j}^N U_{3,ijk}(r_{ij}, r_{jk}, \theta_{ijk}). \quad (2.17)
 \end{aligned}$$

As shown in Figure 2.18, the four-body interaction is highly repulsive at short distances and rapidly decays to zero. We fit the *ab initio* data with

$$\frac{1}{4} U_4(d_l) = g \operatorname{sech}(h d_l), \quad (2.18)$$

where g and h are constants and the factor of $\frac{1}{4}$ accounts for the contribution of four different four-body interactions to the total four-body potential. Values for g and h are given in

Table XIII for the S_4 , Se_4 , and Te_4 clusters.

The case of a heterogeneous four-body cluster could become difficult given the number of different combinations of elements in different positions. We can dramatically simplify this case by assuming that the total four-body interaction is the sum of the four-body contributions of the individual elements in the cluster. For example, the four-body interaction for a S_3Se cluster would be

$$U_4 = 3g_S \operatorname{sech}(h_S d_l) + g_{Se} \operatorname{sech}(h_{Se} d_l), \quad (2.19)$$

and the four-body interaction for a Se_3S cluster would be

$$U_4 = g_S \operatorname{sech}(h_S d_l) + 3g_{Se} \operatorname{sech}(h_{Se} d_l). \quad (2.20)$$

Figure 2.18 shows that this is a reasonable assumption and fits well to the *ab initio* data for heterogeneous clusters. We take $g_{As} = g_{Ge} = 0$.

2.6 Conclusions

We have derived *ab initio* potentials for the S, Se, Te, As, Ge, S-Se, Se-Te, As-Se, Ge-Se, Ge-As, and Ge-As-Se systems using Møller-Plesset perturbation theory and a cluster expansion approach. The interatomic potentials include two-, three-, and effective four-body terms. In the next part of this thesis, we will use these potentials in classical Monte Carlo simulations to investigate the structure of chalcogenide glasses.

Part II

Atomistic Simulations

Chapter 3

Metropolis Monte Carlo

Classical modeling allows for the simulation of much larger systems than what is possible with quantum mechanics alone. Classical atomistic simulations are based on the notion of interatomic potentials, i.e., continuous functions that describe the interactions between atoms. These interatomic potentials can be drawn empirically to reproduce known experimental data, but an *ab initio* approach ensures greater transferability and allows for prediction of material structure and properties without *a priori* knowledge of experimental results. In Part I of this thesis, we used highly accurate quantum mechanical simulations to derive two-, three-, and effective four-body interaction potentials for elemental, binary, and ternary chalcogenide systems. In Part II, we will use these potentials in classical atomistic simulations to compute the structure of various chalcogenide glasses.

The most popular atomistic simulation technique is molecular dynamics,^{60,61} where interatomic potentials are used to compute a net force on each atom. Dividing this force by the mass of the atom yields an acceleration, which is integrated in order to update

atomic velocities and positions. A thermostat is typically employed to maintain a specified temperature through adjustment of the atomic velocities.

Whereas molecular dynamics provides a deterministic method for following atomic trajectories in time, it is not the most efficient technique for computing static properties such as material structure. The Metropolis Monte Carlo technique is an atomistic simulation method that avoids computation of forces and integration of the equations of motion; instead, it relies on generating random configurations of atoms in phase space and using special criteria to determine whether or not to accept each new configuration.⁶² In fact, the name “Monte Carlo” was coined by Metropolis⁶³ owing to the technique’s extensive use of random numbers. By relying on energy calculations and a stochastic sampling process, Metropolis Monte Carlo can provide an equilibrated material structure with much less computation time than traditional molecular dynamics.

In this chapter, we introduce the basic concepts of the Monte Carlo approach, including importance sampling, Markov processes, detailed balance, and acceptance ratios. We derive the Metropolis algorithm and discuss its implementation for the simulation of atomic systems. For additional information on Monte Carlo beyond what is discussed in this chapter, please see the excellent textbook by Newman and Barkema.⁶⁴

3.1 Importance Sampling

Ideally, the expectation value of an arbitrary thermodynamic property, $\langle Q \rangle$, can be calculated by

$$\langle Q \rangle = \frac{\int Q_\lambda e^{-E_\lambda/kT} d\lambda}{\int e^{-E_\lambda/kT} d\lambda}, \quad (3.1)$$

where E is energy, k is Boltzmann's constant, T is absolute temperature, and the integrals are over all possible states of the system. However, in practice it is generally impossible to enumerate every available state of a system, especially for condensed matter. Monte Carlo addresses this issue by choosing a subset of states at random. The average property $\langle Q \rangle$ is approximated by the estimator,

$$Q_M = \frac{\sum_i^M Q_i p_i^{-1} e^{-E_i/kT}}{\sum_i^M p_i^{-1} e^{-E_i/kT}}. \quad (3.2)$$

which samples a total of M states that are chosen with probability distribution p . As the number of sampled states increases, the estimator becomes more and more accurate; in particular,

$$\lim_{M \rightarrow \infty} Q_M = \langle Q \rangle. \quad (3.3)$$

In order to improve the accuracy and convergence of the estimator with smaller values of M , it is necessary to draw random states from an appropriate probability distribution p . If p is chosen to be a uniform distribution over all the available states, the vast majority of chosen states will be highly unfavorable and their contributions to the partition function will be negligible. It is therefore desirable to choose p such that the lower energy states are chosen preferentially. The technique for choosing the important low-energy states from among the very large number of possibilities is known as importance sampling.

In our case, we would like to choose states according to a Boltzmann probability

distribution,

$$p_i = \frac{e^{-E_i/kT}}{\sum_j^M e^{-E_j/kT}}. \quad (3.4)$$

Substituting this probability distribution into the estimator of Equation (3.2) yields

$$Q_M = \frac{\sum_i^M Q_i e^{E_i/kT} e^{-E_i/kT} \sum_j^M e^{-E_j/kT}}{\sum_i^M e^{E_i/kT} e^{-E_i/kT} \sum_j^M e^{-E_j/kT}}, \quad (3.5)$$

where the Boltzmann factors all cancel to give the simple average

$$Q_M = \frac{1}{M} \sum_i^M Q_i. \quad (3.6)$$

This leaves the important question of how we actually choose states such that they follow the Boltzmann probability condition of Equation (3.4). In Metropolis Monte Carlo, this is accomplished by generating a Markov chain of states and using the criterion of detailed balance.

3.2 Markov Processes and Detailed Balance

A Markov process is a mechanism for generating a new state j based only on the current state i , and not on any of the previous states. The transition probability from state i to state j is denoted $P(i \rightarrow j)$ and satisfies the constraint

$$\sum_j P(i \rightarrow j) = 1. \quad (3.7)$$

Note that the transition probability $P(i \rightarrow i)$, which is the probability of remaining in the original state i , may be nonzero.

With Metropolis Monte Carlo, we use the Markov process repeatedly to generate a Markov chain of states. In other words, starting from a state i , the Markov process is used to generate a new state j . This new state is used again in the Markov process to generate another new state. This process continues until we have generated a sequence of states that appear with the desired probability distribution, i.e., the Boltzmann distribution. When this occurs, we are said to have “reached equilibrium,” and the estimator can then be calculated according to Equation (3.6).

This process assumes the condition of ergodicity, i.e., it must be possible for the Markov process to reach any state of the system from any other state if we let it run for long enough. While we can make some of the transition probabilities zero, there must be at least one path of nonzero probability between any two states of the system.

The other necessary condition for achieving equilibrium is that of detailed balance,

$$p_i P(i \rightarrow j) = p_j P(j \rightarrow i), \quad (3.8)$$

where the probability of transition from state i to state j is equal to that of the reverse transition. Since we wish the equilibrium distribution to satisfy the Boltzmann condition of Equation (3.4), the detailed balance equation should satisfy

$$\frac{P(i \rightarrow j)}{P(j \rightarrow i)} = \frac{p_j}{p_i} = e^{-(E_j - E_i)/kT}. \quad (3.9)$$

If Equations (3.7) and (3.9) are satisfied, as well as the condition of ergodicity, then we have generated an equilibrium chain of states following the desired Boltzmann probability distribution.

3.3 Acceptance Ratios

The trick to actually achieving these criteria is to break the transition probability into two parts,

$$P(i \rightarrow j) = g(i \rightarrow j) A(i \rightarrow j), \quad (3.10)$$

where $g(i \rightarrow j)$ is the selection probability, which is the probability that our Monte Carlo algorithm will generate a new target state j starting from state i , and $A(i \rightarrow j)$ is the acceptance probability or acceptance ratio. The acceptance ratio states that if we start in some state i and the algorithm generates a new state j , this new state should only be accepted with a probability $A(i \rightarrow j)$; otherwise, the system should remain in the original state i . With this definition, Equation (3.9) becomes

$$\frac{P(i \rightarrow j)}{P(j \rightarrow i)} = \frac{g(i \rightarrow j) A(i \rightarrow j)}{g(j \rightarrow i) A(j \rightarrow i)} = e^{-(E_j - E_i)/kT}. \quad (3.11)$$

In Metropolis Monte Carlo, new states are generated with an equal probability distribution, i.e., $g(i \rightarrow j) = g(j \rightarrow i)$ such that

$$\frac{P(i \rightarrow j)}{P(j \rightarrow i)} = \frac{A(i \rightarrow j)}{A(j \rightarrow i)} = e^{-(E_j - E_i)/kT}. \quad (3.12)$$

Therefore, the task of achieving the desired Boltzmann distribution is left to proper choice of acceptance ratios. In Metropolis Monte Carlo, the acceptance ratio is chosen to be

$$A(i \rightarrow j) = \begin{cases} e^{-(E_j - E_i)/kT}, & \text{if } E_j - E_i > 0 \\ 1, & \text{otherwise.} \end{cases} \quad (3.13)$$

In other words, any transition that lowers the energy of the system is always accepted, and any transition that increases the energy of the system is accepted according to a Boltzmann probability. Note that this choice of $A(i \rightarrow j)$ satisfies the condition of Equation (3.12).

3.4 The Metropolis Algorithm

The Metropolis algorithm for implementing the above Monte Carlo scheme consists of the following steps:

1. Compute the energy of the current state, E_i .
2. Generate a new state according to the Markov process. In the canonical ensemble, this is accomplished by choosing a random atom in the system and assigning it a random displacement. (In an isobaric ensemble, a new state can also be generated by changing the volume of the system. In an open ensemble, new states may also involve randomly creating or annihilating atoms. For more information on using Monte Carlo with these alternative ensembles, see Allen and Tildesley.⁶¹)
3. Compute the energy of the new state, E_j .
4. If $E_j \leq E_i$, accept the new state. If $E_j > E_i$, draw a random value from a uniform

distribution between 0 and 1. If this random value is less than $e^{-(E_j-E_i)/kT}$, then the new state is accepted; otherwise, return the system to the original state.

5. Repeat steps 1-4 until the energy of the system has converged to an equilibrium value.

Please note that in the canonical ensemble the temperature of the system is held constant. In this case, the average kinetic energy of the system is the same for all states, so the difference in internal energy between states is equal to the difference in potential energy only:

$$E_j - E_i = U_j - U_i. \quad (3.14)$$

Hence, unlike molecular dynamics, the Monte Carlo technique does not involve calculation of atomic momenta. This effectively reduces the phase space dimensionality from $6N$ to $3N$, where N is the total number of particles in the system.

In the next chapter we introduce Molsym, an object-oriented program that implements the above Metropolis Monte Carlo algorithm. This algorithm is used together with our *ab initio* interatomic potentials from the previous chapter to compute the structure of chalcogenide glasses.

Chapter 4

Molsym: An Object-Oriented Platform for Atomistic Simulations

Molsym is a new program we have developed for classical atomistic simulations. The program is a unified, object-oriented platform for a variety of simulation techniques, including molecular dynamics, Metropolis Monte Carlo, and mapping of energy landscapes using eigenvector-following. In this chapter, we give an overview of the design philosophy behind Molsym and provide details on some of the key components of the program.

4.1 Design Philosophy

Object-oriented design is a computer programming paradigm where software is composed of a set of individual objects or data structures; this is in contrast to the traditional view in which software is simply a list of instructions to be executed by the computer. Object-oriented design allows for much greater modularity and extensibility compared to

traditional procedural programming. Objects are created, or instantiated, from a class. A class defines all of the properties and behaviors that an object should have. For example, if we wish to model a door, we could create a class that has data members for such properties as height, width, type of doorknob, etc. The behaviors, or functions, would include the ability for the door to open, close, lock, and unlock. Once the door class is defined, any number of door objects can be instantiated, each with different properties but similar behaviors. In the case of Molsym we define a variety of classes to describe different aspects of an atomistic simulation. Some of the key classes in Molsym are discussed in Section 4.2.

One of the greatest advantages of object-oriented design is that it facilitates code reusability. For example, Molsym supports a variety of different solvers, including molecular dynamics, Monte Carlo, and eigenvector-following. All these techniques are based on having a set of atoms defined in a simulation space, where the interactions are described by a set of potentials. The atoms, the simulation space, and the interatomic potentials are common to all three solvers. With object-oriented programming, the same classes are used to define the common elements of the simulation, and different solver classes can be substituted to change the computational behavior of the simulation.

The idea of having different variations on a common theme, e.g., different types of solvers that act differently on the same system, is facilitated through the concept of inheritance. For example, if we want to model living organisms we can define an abstract base class for an arbitrary organism. This base class would contain elements that are common to all organisms, including data members for DNA and cellular structure and functions for nutrition and reproduction. We can then derive new classes from the base

organism class, e.g., a plant class or an animal class. These subclasses inherit all of the data members and functions of the base class, but they also define new data members and functions that are specific to the subclass. For example, the plant class would have a function for photosynthesis that is not found in the animal class, and the animal class would have a function for locomotion that is not available to plants. New subclasses can also be defined from the existing subclasses, e.g., separate fish, bird, and mammal classes could be derived from the animal class. These new classes inherit the data members and functions from all classes above them in the hierarchy.

Another important concept in object-oriented design is polymorphism, where the same function can produce different behaviors depending on the particular subclass from which it is called. In our example of living organisms, the functions of the base organism class can be overloaded to define more specific behavior. For instance, the reproduction function can be overloaded to define mitosis behavior in a bacterium class or sexual reproduction in an animal class. When the reproduction function is called for an arbitrary organism object, polymorphism enables the organism to “know” specifically how it is supposed to reproduce.

In the case of Molsym, we define an abstract base class for an arbitrary solver object. This solver class contains a “run” function that is overloaded to produce specific behavior in the molecular dynamics and Monte Carlo subclasses. The program requires a pointer to an arbitrary solver object, and when the “run” function is called, polymorphism allows the correct algorithm to be executed depending on particular type of solver.

Object-oriented programming also allows for operator overloading, where functions

are defined in a class for describing addition using the `+` operator, multiplication using the `*` operator, and so on. For instance, Molsym defines a **Coordinates** class that represents a vector in three-dimensional space. The various operators are overloaded to provide a convenient way of doing vector arithmetic using the standard `+`, `*`, and other operators.

Molsym is written entirely in ANSI-standard C++, which allows for portability across different operating systems and chip architectures. We have compiled and run Molsym on a PowerPC architecture under Mac OS X, an Alpha architecture under Tru64 UNIX, and AMD/Intel architectures running Red Hat Linux.

4.2 Class Structure

Figure 4.1 shows the class hierarchy for Molsym. Each box represents a separate class, and the abstract base classes are indicated by a dashed outline. The arrows indicate inheritance; for example, the **MonteCarlo** class inherits from the abstract **Solver** class, and the **Nanoindentation** class inherits from **MonteCarlo**. In this section, we provide a brief description of the important classes in Molsym. For more information on specific details of implementation, please contact the author.

4.2.1 Application and Simulation Classes

The **Application** class is an abstract base class that provides basic functions for initializing, running, and terminating a computer program. **Application** also includes exception handling capabilities to handle possible errors such as division by zero. The **Simulation** class derives all of these behaviors from **Application** and includes all of the

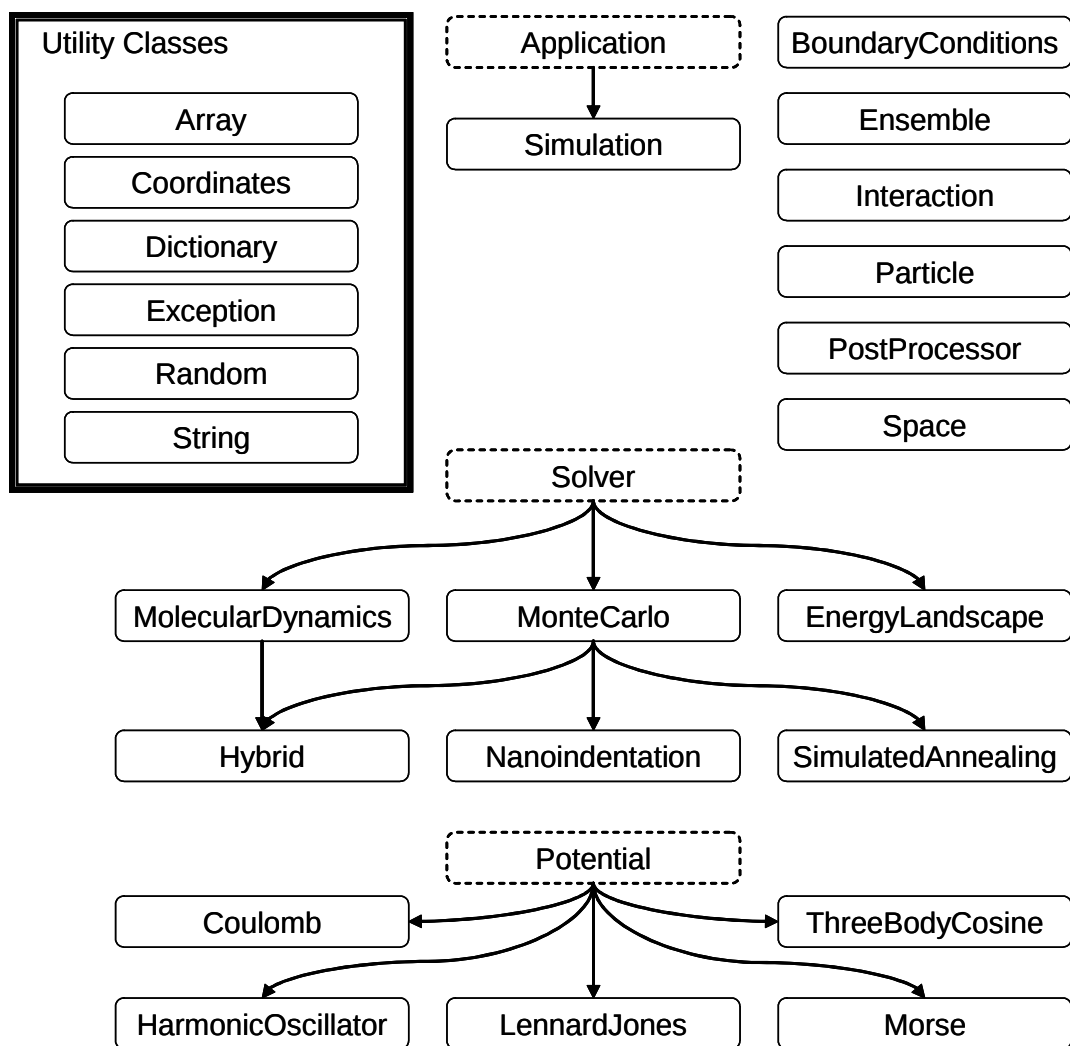


Figure 4.1. Molsym class hierarchy. Abstract base classes are shown with a dashed outline.

data members and functions specific to classical atomistic simulations. Data members include a **Space** object to define the simulation space, with the appropriate **BoundaryConditions**. An **Ensemble** object defines the statistical mechanical ensemble, and an array of **Particle** objects explicitly defines each atom and its properties. The **Simulation** class also includes an array of **Interaction** objects to define the atomic interactions. Finally, a **Solver** class defines the computation mode for the simulation. More details on these classes are provided in the ensuing subsections.

4.2.2 Space Class

The **Space** class defines the dimensions of the simulation cell. The simulation cell is assumed to be a rectangular prism with associated boundary conditions.

4.2.3 BoundaryConditions Class

The **BoundaryConditions** class defines the boundary conditions for the simulation cell. Options include periodic boundary conditions, fixed wall boundaries, or open boundaries. These can be chosen independently for the xy , xz , and yz planes of the simulation cell. The class also contains functions for computing the shortest distance between two atoms accounting for the specified boundary conditions.

4.2.4 Ensemble Class

The **Ensemble** class specifies the statistical mechanical ensemble of the system. Choices include canonical (NVT), isothermal-isobaric (NPT), grand canonical (μVT), and Gibbs (μPT). The microcanonical (NVE) ensemble is also available for molecular dynam-

ics simulations.

4.2.5 Particle Class

The `Particle` class defines a single atom (or larger particle unit). Data members include a particle name, mass, position, velocity, acceleration, and a list of neighbor particles. Functions in the `Particle` class allow for calculation of kinetic and potential energies, movement of the particle, and updating of the neighbor list.

4.2.6 Interaction Class

The `Interaction` class defines a matrix of `Potential` objects to describe the potentials for all combinations of particle types. The interactions can be one-body (e.g., the potential in an electric field), two-body, or three-body.

4.2.7 Potential Classes

The `Potential` class is an abstract base class for defining individual potential interactions. It contains a “calculate” function that can be overloaded for each specific type of interaction. We have defined subclasses for `Coulomb`, `HarmonicOscillator`, `LennardJones`, `Morse`, and `ThreeBodyCosine` potentials, among others.

4.2.8 Solver Classes

The `Solver` class is an abstract base class for defining different types of classical solvers, such as `MolecularDynamics` and `MonteCarlo`. The `Hybrid` solver inherits functions from both the `MolecularDynamics` and `MonteCarlo` solvers to allow for molecular

dynamics time steps interspersed with Monte Carlo displacements. The **EnergyLandscape** solver implements the eigenvector-following techniques discussed in Part III of this thesis. The **Nanoindentation** solver is a specific implementation of MonteCarlo that allows for the loading and unloading of a hard-shell spherical indenter at a surface. Finally, the **SimulatedAnnealing** class implements a version of MonteCarlo where the temperature is decreased throughout the course of the simulation. Each of these subclasses overloads the **Solver** run function in order to provide the computational behavior for that specific type of solver.

4.2.9 PostProcessor Class

The **PostProcessor** class allows for calculation of structural properties such as pair distribution functions, bond angle distributions, bond type distributions, and chain/ring length distributions.

4.2.10 Utility Classes

Molsym has several utility classes, including an **Array** class for generating dynamical arrays of arbitrary objects. The **Coordinates** class is used for representing vectors in three-dimensional space and includes functions and operator overloading for all types of vector operations. The **Dictionary** class is similar to **Array**, except that the elements of a **Dictionary** object are accessed through keys instead of through an index number. The **Exception** class enables detailed exception handling for locating errors in the code. The **Random** class includes functions for generating random numbers according to uniform, Gaussian, and Poisson distributions. Finally, the **String** class contains many features for

easy input, output, and manipulation of character strings.

4.3 Optimization Techniques

Molsym includes many optimization techniques to increase computational efficiency. For example, each **Particle** object includes a list of neighbors within a specified cutoff distance. When computing the potential energy of the particle, it considers only those particles within this list of neighbors. The neighbor list is automatically updated when an atom moves a total distance of more than half the cutoff value.

In order to further reduce computation time, interatomic potentials are precomputed on a fine grid when the program first initializes. This grid is fit to a cubic spline such that potential calculations involve only array lookups and simple multiplication rather than evaluation of the full expressions, which are more computationally intensive. Molsym also takes advantage of symmetries in the two- and three-body interactions in order to further increase computational efficiency.

Another technique for reducing computation time is to avoid square root calculations wherever possible. For example, comparing square distances instead of distances eliminates two square root operations without detracting from the intended purpose of the computation.

Finally, Molsym takes advantage of a number of compiler optimizations that maximize computational efficiency for a given chip architecture and operating system.

Chapter 5

Chalcogenide Glass Structure

Over seventy years have passed since the publication of Zachariasen’s landmark 1932 paper on glass structure,⁶⁵ which he began by acknowledging, “It must be frankly admitted that we know practically nothing about the atomic arrangement in glass.” While our knowledge has certainly grown enormously in the ensuing decades,⁶⁶ many aspects of glass and glass structure still remain a mystery.

Whereas Zachariasen’s rules for glass formation⁶⁵ focus on oxide glasses, the Phillips topological constraints model^{67–69} addresses glass formability and structure in covalently bonded materials such as chalcogenides. According to the Phillips theory, glass-forming ability is determined by comparing the number of atomic degrees of freedom with the number of interatomic force field constraints.⁶⁷ If the number of degrees of freedom is greater than the number of constraints the network becomes “floppy,” a condition which facilitates rearrangement of atoms into a minimum energy configuration, i.e., a crystalline structure. Conversely, if the network becomes overconstrained, rigid structures will percolate through-

out the entire body which can lead to crystallization.⁷⁰⁻⁷⁴ Phillips conjectured that the tendency for glass formation would hence be maximized when the number of degrees of freedom equals the number of constraints.⁶⁷

$$M_d = M_c. \quad (5.1)$$

Accounting for two- and three-body force fields, the number of constraints is

$$M_c = \sum_{i=1}^N \left[\frac{m_i}{2} + (2m_i - 3) \right], \quad (5.2)$$

where the system contains N atoms and m_i is the coordination number of the i^{th} atom.

The number of degrees of freedom in the system is

$$M_d = 3N. \quad (5.3)$$

Equating M_c and M_d , and averaging over all atoms, we obtain

$$\frac{m_c}{2} + (2m_c - 3) = 3, \quad (5.4)$$

where m_c is the critical average coordination number of atoms. This yields

$$m_c = 2.4. \quad (5.5)$$

Thus, according to the Phillips model the optimum condition for glass formation occurs

when the average coordination number of the constituent atoms realizes a critical value of $\langle R \rangle = R_c = 2.4$.^{71,75}

The average coordination number itself is defined as

$$\langle m \rangle = \sum_i x_i m_i \quad (5.6)$$

where x_i is the mole fraction of the i^{th} constituent element of the material. The coordination number of each element is given by $m_i = 8 - N_i$, where N_i is the number of valence electrons. Thus, the Group VI chalcogen elements (e.g., sulfur, selenium, and tellurium) have a coordination number of $m_{VI} = 2$. Similarly, the coordination number of Group V elements (e.g., arsenic and antimony) is $m_V = 3$, and the coordination of Group IV elements such as germanium is $m_{IV} = 4$. Chalcogenide glasses are often binary, ternary, or even quaternary compounds of these elements, but by definition they must contain at least one chalcogen element.

In order to determine the validity of the Phillips model, many researchers have sought correlation between measured values of thermal and mechanical properties and the average coordination number of chalcogenide glass compositions. Measurement of elastic constants in the Ge-As-Se system by Halpapp and Lindsay⁷⁶ showed evidence of rigidity percolation at $\langle m \rangle = 2.4$. In addition, Mössbauer experiments by Bresser *et al.*⁷⁷ showed microscopic structural changes consistent with the Phillips model.

Swiler *et al.*⁷⁸ experimentally prepared thirty-six compositions in the Ge-Sb-Se ternary system and performed Vickers microhardness and surface toughness measurements on the resulting samples. Their results show that while hardness increases linearly with

the average coordination number $\langle m \rangle$ of the glass, surface toughness displays a distinct maximum at $\langle m \rangle \approx 2.6$. Sreeram *et al.*⁷⁹ extended this study to include arsenic and tellurium and found a similar trend for hardness as a function of $\langle m \rangle$. However, an ensuing study by Senapati *et al.*⁸⁰ of Ge-Sb-Se and Ge-Se systems showed a maximum in the Vickers hardness number at $\langle m \rangle = 2.67$.

Sreeram *et al.*⁸¹ also used experimental data to develop an empirical relationship between glass transition temperature T_g and average coordination number $\langle m \rangle$. Their results show that T_g increases monotonically with $\langle m \rangle$, which suggests that there is no fundamental change in bonding at $\langle m \rangle = 2.4$. However, another study by Sreeram *et al.*⁸² shows that the molar volume of chalcogenide glasses does exhibit a clear minimum at $\langle m \rangle = 2.4$, notwithstanding that the measured values of elastic moduli do not show any significant change at this point.

Subsequent experiments on Ge-Se and Ge-Sb-Se systems by Senapati and Varshneya⁸³ confirmed a relative minimum in molar volume at $\langle m \rangle = 2.4$ and also found minima in liquid-state heat capacity and thermal expansion coefficient at this same point. Coupled with measurements of the glassy-state heat capacity and thermal expansion coefficient, Senapati and Varshneya determined that the configurational contribution to these two properties (i.e., the change in these properties associated with glass transition) is at a minimum in chalcogenide glasses with $\langle m \rangle = 2.4$. These results suggest that structural rearrangements in the liquid state are minimized at $\langle m \rangle = 2.4$, thereby minimizing the propensity for crystallization. Thus compositions with this average coordination number are the best glassformers, exhibiting the greatest yield strength and lowest plasticity.⁸⁴ In another pa-

per, Senapati and Varshneya⁸⁵ discuss how this result demonstrates an anomaly in the traditional classification of “strong” and “fragile” liquids put forth by Angell.^{86–89} The relationship between the Phillips and Angell theories has also been shown by Tatsumisago *et al.*⁹⁰ for the Ge-As-Se system, but without the observed anomaly of Senapati and Varshneya.

While the experiments of Varshneya and coworkers^{78–85} focused on the behavior of chalcogenide glass properties around $\langle m \rangle = 2.4$, Tanaka⁹¹ found that the molar volume of the Ge-As-S ternary system exhibits two distinct thresholds: a minimum at $\langle m \rangle = 2.4$ and a maximum at $\langle m \rangle = 2.67$. Tanaka hypothesized that these critical values of average coordination number correspond to changes in the dimensionality of the glass network; specifically, at $\langle m \rangle = 2.4$ the glass transitions from a one-dimensional to a two-dimensional structure, and at $\langle m \rangle = 2.67$ the glass network becomes three-dimensional. Narayanan and Kumar⁹² suggested that this second threshold is where the bonds in the glass system become completely heteropolar, i.e., all bonding is between unlike atoms (Ge-S, not Ge-Ge).

However, Sen and coworkers^{93,94} effectively refuted this argument by finding homopolar bonding in Ge-As-S glasses with deficient sulfur. While the bonding was completely heteropolar in the stoichiometric system, As-As and then Ge-Ge bonds were found with decreasing sulfur content. Additional experiments on Ge-As-S glasses by Aitken and Ponader^{95,96} found that thermal expansion coefficient and molar volume are both maximized at $\langle m \rangle = 2.6$, but they found no evidence of any threshold at $\langle m \rangle = 2.4$.

In order to explain these and other similar results,⁹⁷ Narayanan⁹⁸ introduced a variation of the chemically ordered covalent network model in which homopolar bonding

Table XIV. Color Key for Structure Plots

Element	Color
Sulfur	Yellow
Selenium	Gray
Tellurium	Blue
Arsenic	Red
Germanium	Purple

is also considered. Homopolar bonding can result in the formation of elemental clusters within the glass structure that may shift the Tanaka chemical threshold from $\langle m \rangle = 2.67$ to $\langle m \rangle = 2.6$ or even as low as $\langle m \rangle = 2.4$. Narayanan maintained that the best glass formation occurs near the rigidity percolation threshold ($\langle m \rangle = 2.4$), and compositions near the chemical threshold ($\langle m \rangle = 2.67$ or less) are poor glass formers. Narayanan subsequently demonstrated the utility of his model by accurately predicting the phase diagrams of several chalcogenide glass systems.⁹⁹ The idea of clustering in chalcogenide glasses leading to non-ideal behavior has also been put forth by Thorpe *et al.*¹⁰⁰ and experimentally investigated by Boolchand and coworkers.^{101–104} An additional modification to the theory of covalent network glass structure includes the possibility of one-fold coordinated atoms,^{105–109} as would occur in chalcohalide glasses.

While laboratory experiments are essential for confirming or refuting any theory, additional physical insight may be gained through modeling and simulation. In this chapter, we use our *ab initio* interatomic potentials from Part I in classical Monte Carlo simulations to characterize the structure of elemental, binary, and ternary chalcogenide glasses. Glass structures are shown using the color key in Table XIV.

5.1 Elemental Glasses

We begin our simulations by placing 1000 atoms at random positions in a cubic, isochoric simulation space with periodic boundary conditions. The densities of the S, Se, and Te systems are fixed at 1.75, 4.30, and 5.90 g/cm³, respectively, and we consider a constant temperature of $T = 200$ K for sulfur and $T = 298$ K for selenium and tellurium. The trial displacements are made by assigning a random move along each of the three global axes, $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$, where the probability density function is Gaussian with zero mean and a standard deviation of σ . We simulate a total of 20 million trial displacements with a target acceptance rate of 40%. The magnitude of σ is dynamically adjusted during the simulation to achieve this acceptance rate.

Since our cluster expansion approach to potential development is based on energies computed for small isolated clusters of atoms, it is desirable to test the validity of these potentials in an extended, three-dimensional solid. While we have accurately included interactions up to the fourth order, higher order interactions, if significant, could change the overall cohesive energy of a solid system. We have computed a cohesive energy of 2.258 eV/atom for pure selenium glass using our two-, three-, and effective four-body potentials. This is in excellent agreement with experimental values, which range from about 2.25 to 2.35 eV/atom, depending on the defect concentration in the glass.^{110,111} Therefore, we may gain confidence in our cluster expansion method and the truncation of higher order interaction terms.

Pictures of the final S, Se, and Te glass structures are shown in Figures 5.1-5.6, where we can see that the structures are dominated by many kinked, tangled chains of

atoms. The pair distribution functions¹¹² for the elemental glasses are given in Figures 5.7-5.9. From these figures, we can see that the nearest-neighbor distance is well-defined in all cases. The second- and third-nearest neighbor positions are more diffuse owing to the bond angle distributions, also shown in Figures 5.7-5.9, which are centered around 110-120°. Bond angles in the 110-120° range are expected based on the three-body potentials in Figure 2.3. The pair distribution functions show that the glassy structures become completely disordered after about 7 Å.

Whereas liquid sulfur is known to be composed largely of S₈ rings, the structure of sulfur glass is not well-characterized since sulfur glasses are highly unstable. However, a recent experimental study by Kalampounias, Kastrissios, and Yannopoulos¹¹³ has determined that the dominant features in sulfur glass are likely to be S_n chains in addition to a reduced fraction of S₈ rings. This notion is supported by the empirical modeling of Popescu,¹¹⁴ who found that glassy sulfur is composed of a random mixture of short S_n chains and rings. As shown in Figure 5.7(d), our modeling predicts that sulfur glass is dominated by S_n chains with an average length of $\langle n \rangle = 156$ atoms; however, we do not observe many ring structures. This lack of ring structures was also observed in the empirical modeling of Kastowsky and Bradaczek.¹³ The difference between modeling and experiment in this matter could be related to the simulation method or the large experimental uncertainty. However, it is likely that the thermal history and processing of sulfur play a large role in determining the final structure: glasses prepared by melting and then quenching crystalline sulfur at a lower temperature could be more likely to have S₈ rings than those prepared by other methods, e.g., vapor deposition or the quenching of liquid

sulfur from a high temperature.¹¹⁵ In other words, it is possible that the S₈ ring structures observed by Kalampounias *et al.*¹¹³ are artifacts of their particular glass-forming process; the Monte Carlo method used by Kastowsky and Bradaczek¹³ and in this work could better approximate the latter case of vapor deposition or high temperature quenching, where the initial configuration has a higher degree of disorder. Further experimental and modeling work is required in order to clarify this point.

Our calculated pair distribution function for selenium glass in Figure 5.8(a) is in very good agreement with the semi-empirical modeling of Caprion and Schober¹⁵ and that of Molina, Lomba, and Kahl.¹¹⁶ However, our bond angle distribution is in disagreement with Molina and coworkers, who predict a distribution centered at about 100°. The preferred experimental bond angle is about 115°,¹⁴ which is in good agreement with our modeling results in Figure 5.8(b). As shown in Figure 5.8(c), the defect concentration in our selenium glass, i.e., the fraction of atoms with an “incorrect” coordination, is about 7.5%. This is less than a quarter of the defect concentration found by Molina and coworkers¹¹⁶ in their semi-empirical modeling. Again, our results are in better agreement with experiment, which predicts a structure dominated by long, two-coordinated chains of selenium atoms.^{117–120} We also find the presence of large rings containing hundreds of atoms.

Similar structural data are shown in Figure 5.9 for elemental Te glass. The pair distribution function in Figure 5.9(a) predicts well-defined first and second neighbor distances and complete amorphism after about 7 Å. These features are in very good agreement with neutron scattering data¹²¹ for liquid tellurium. The bond angle distribution in Figure 5.9(b) consists of a broad peak centered around 110°. This distribution is significantly

broadener than for selenium. The coordination number distribution for Te glass is plotted in Figure 5.9(c), assuming a bond cutoff distance of 3.0 Å. We find that 91.4% of atoms are two-coordinated, leading to long chains of atoms similar to that found in Se glass, a result which is in good qualitative agreement with neutron scattering studies.¹²² Comparing Figure 5.9(d) with Figure 5.8(d), we note that the atomic chains in Te glass are significantly shorter than those in Se glass; moreover, ring structures are almost completely absent in Te glass.

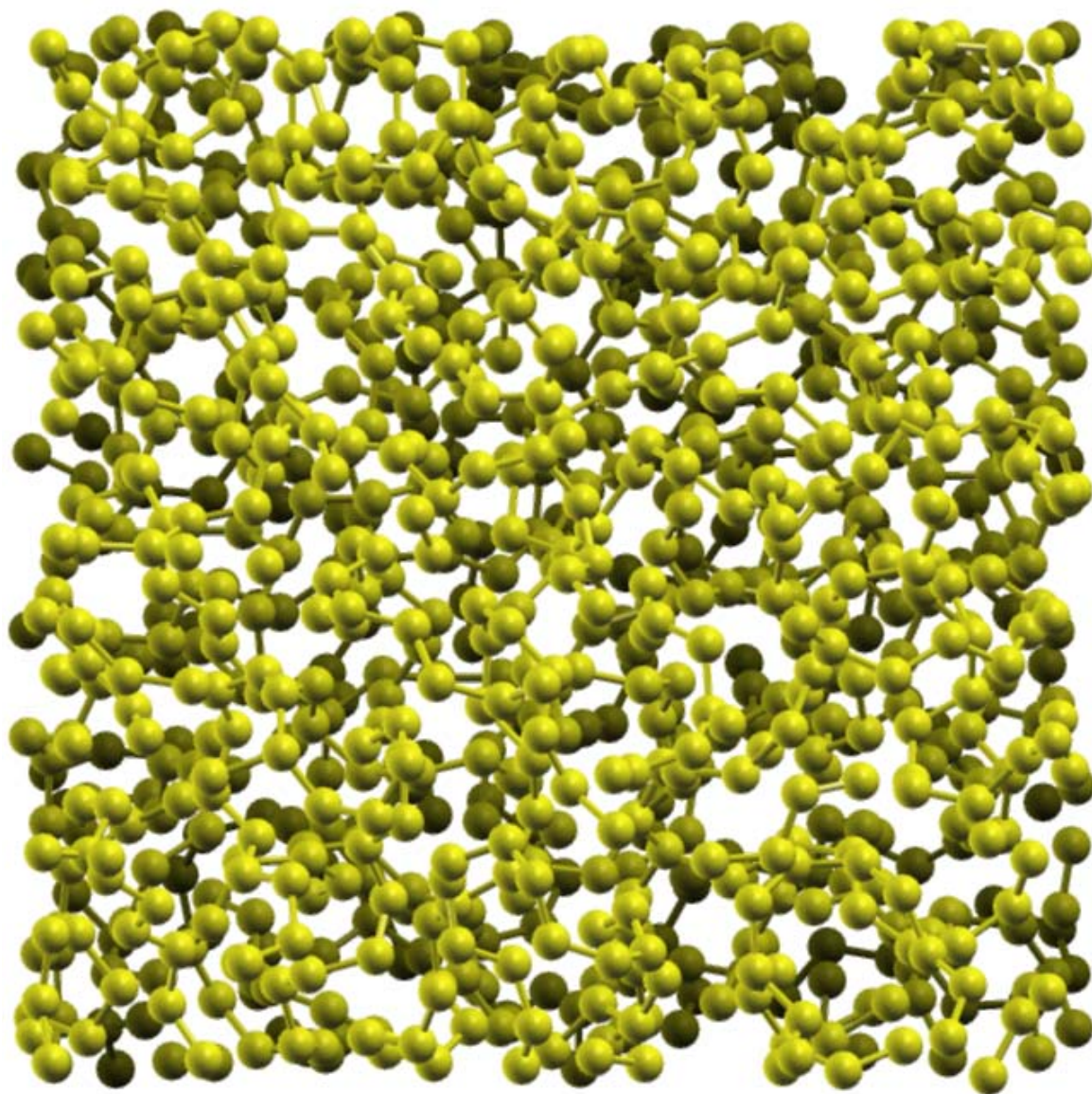


Figure 5.1. Computed structure of sulfur glass.

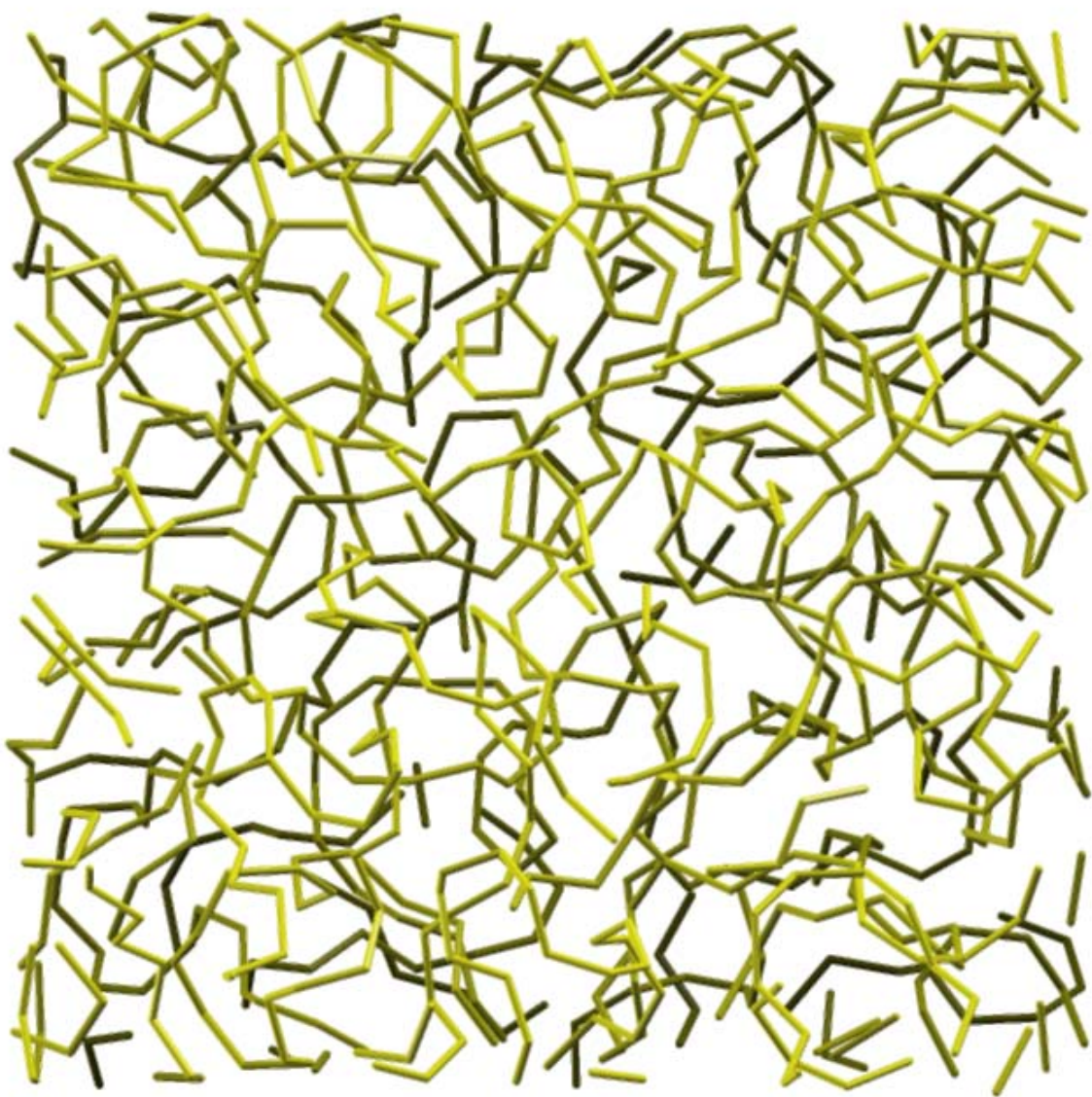


Figure 5.2. Computed structure of sulfur glass (stick representation).

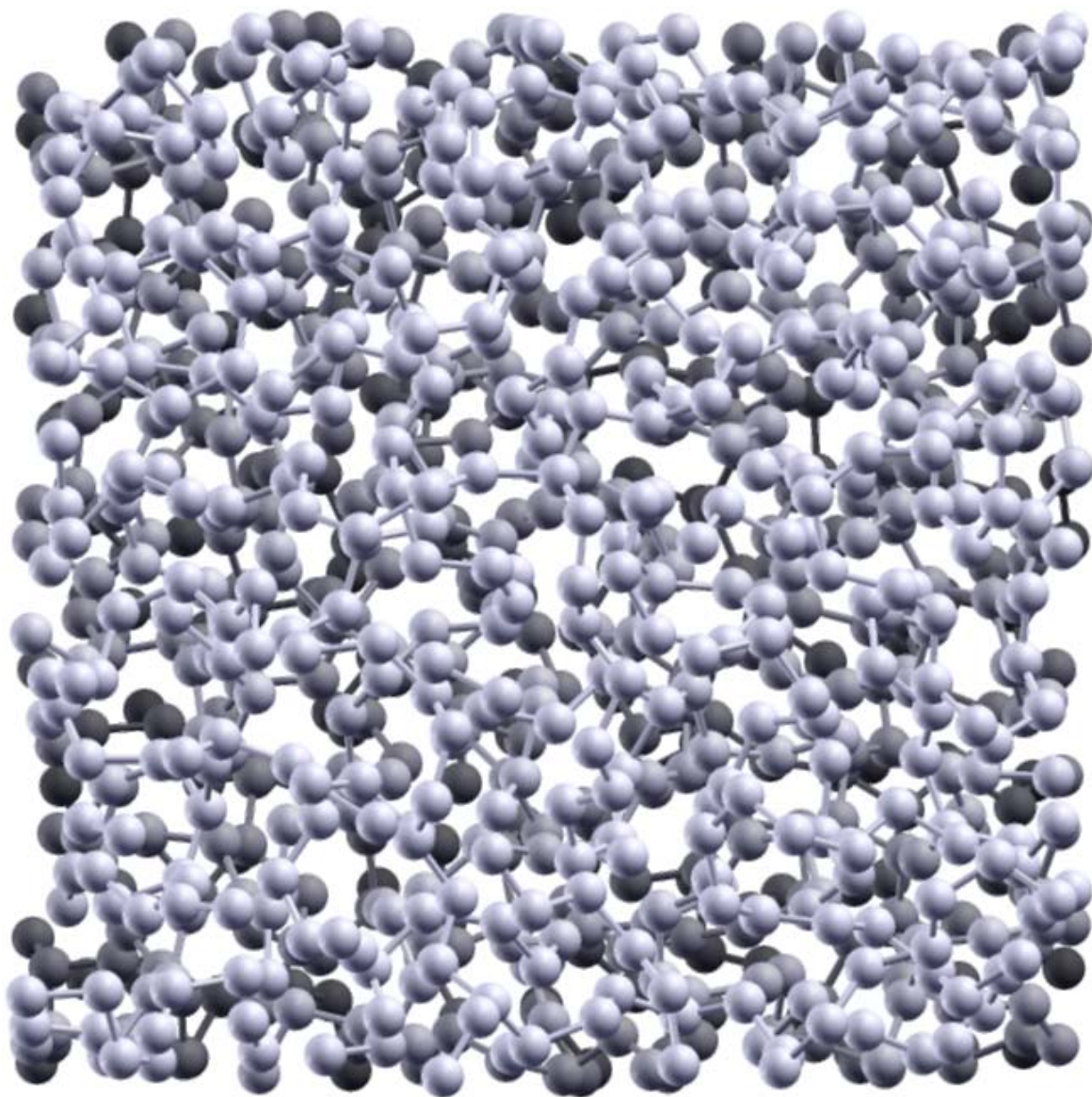


Figure 5.3. Computed structure of selenium glass.

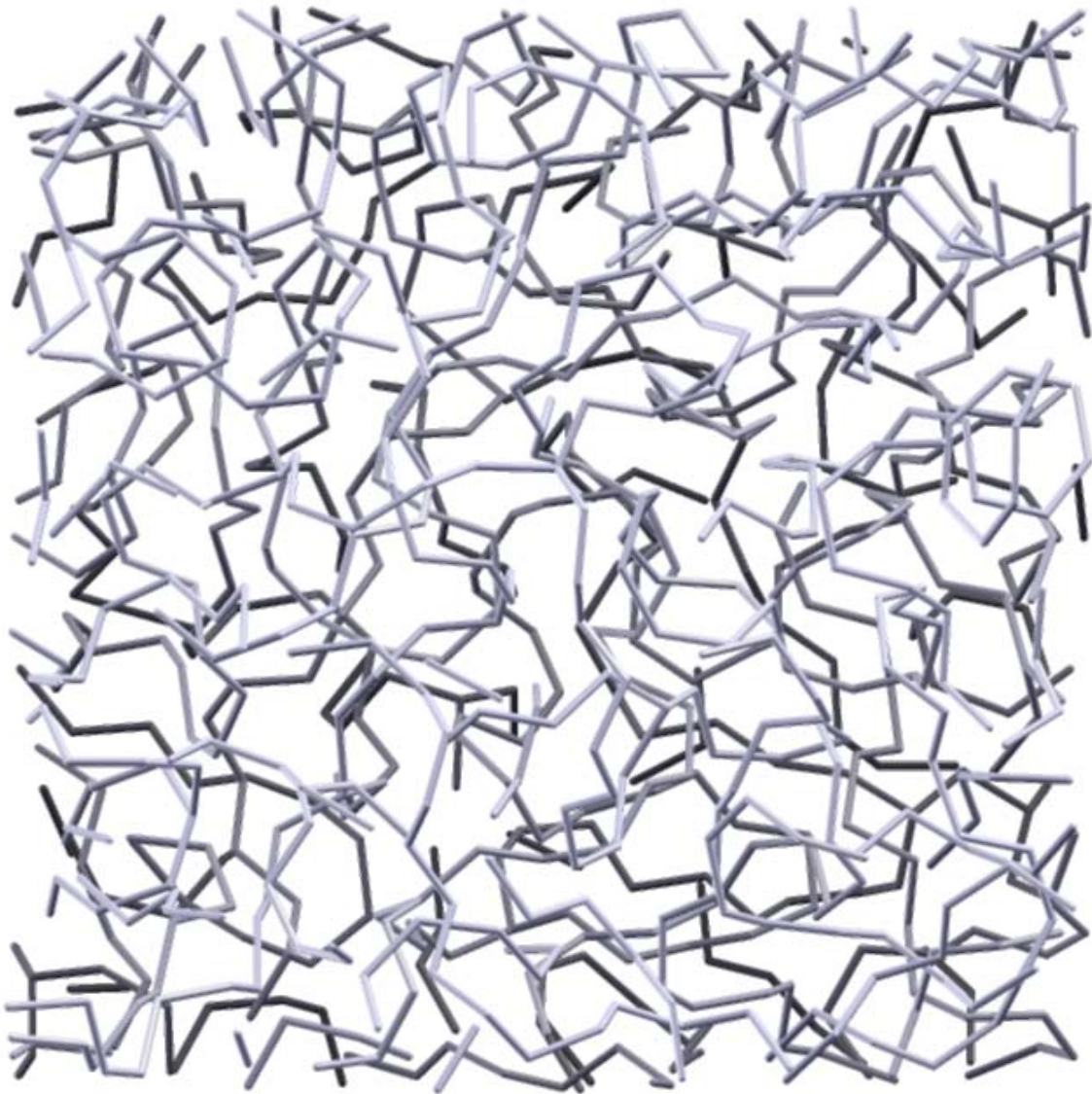


Figure 5.4. Computed structure of selenium glass (stick representation).

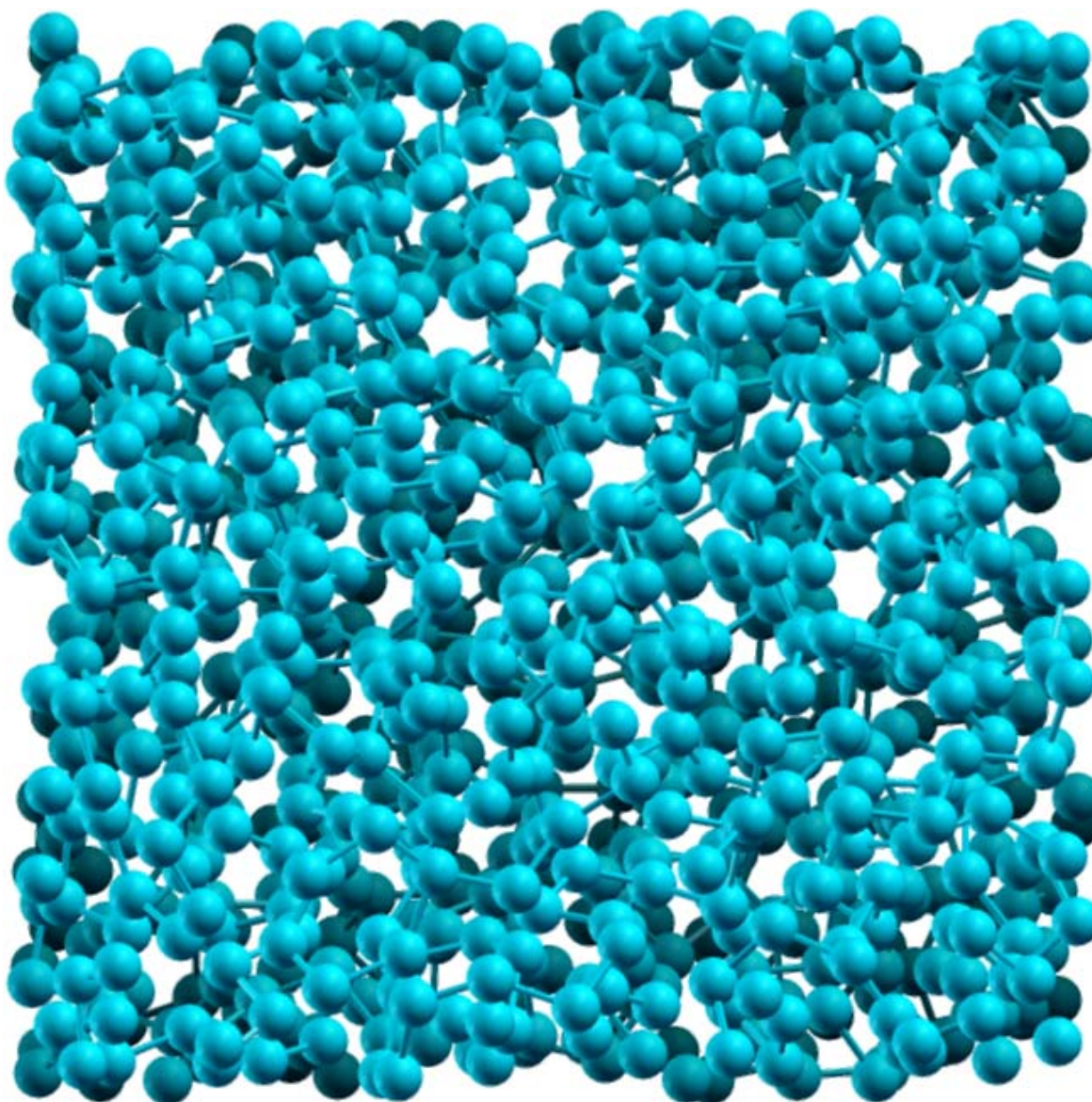


Figure 5.5. Computed structure of tellurium glass.

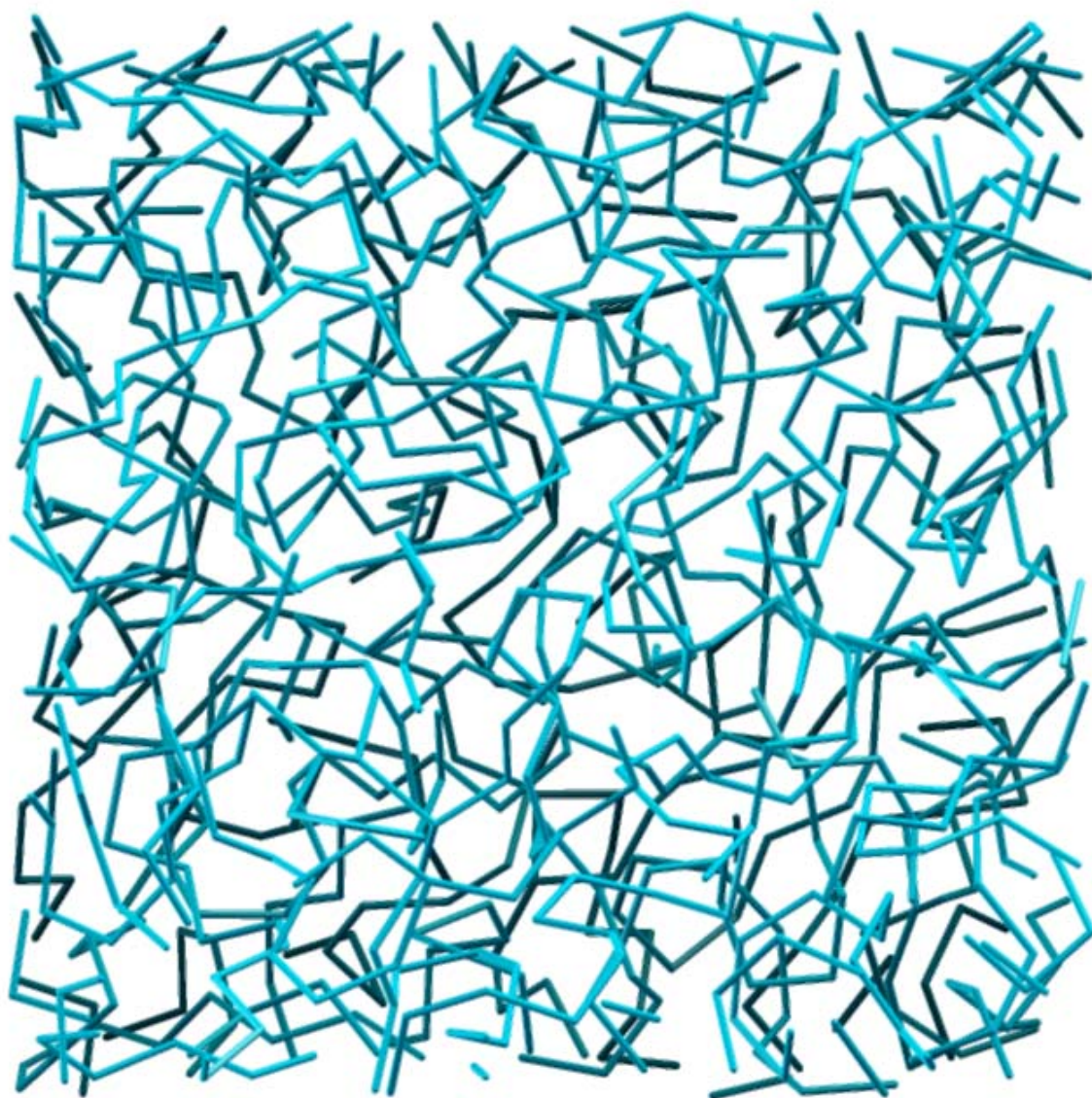


Figure 5.6. Computed structure of tellurium glass (stick representation).

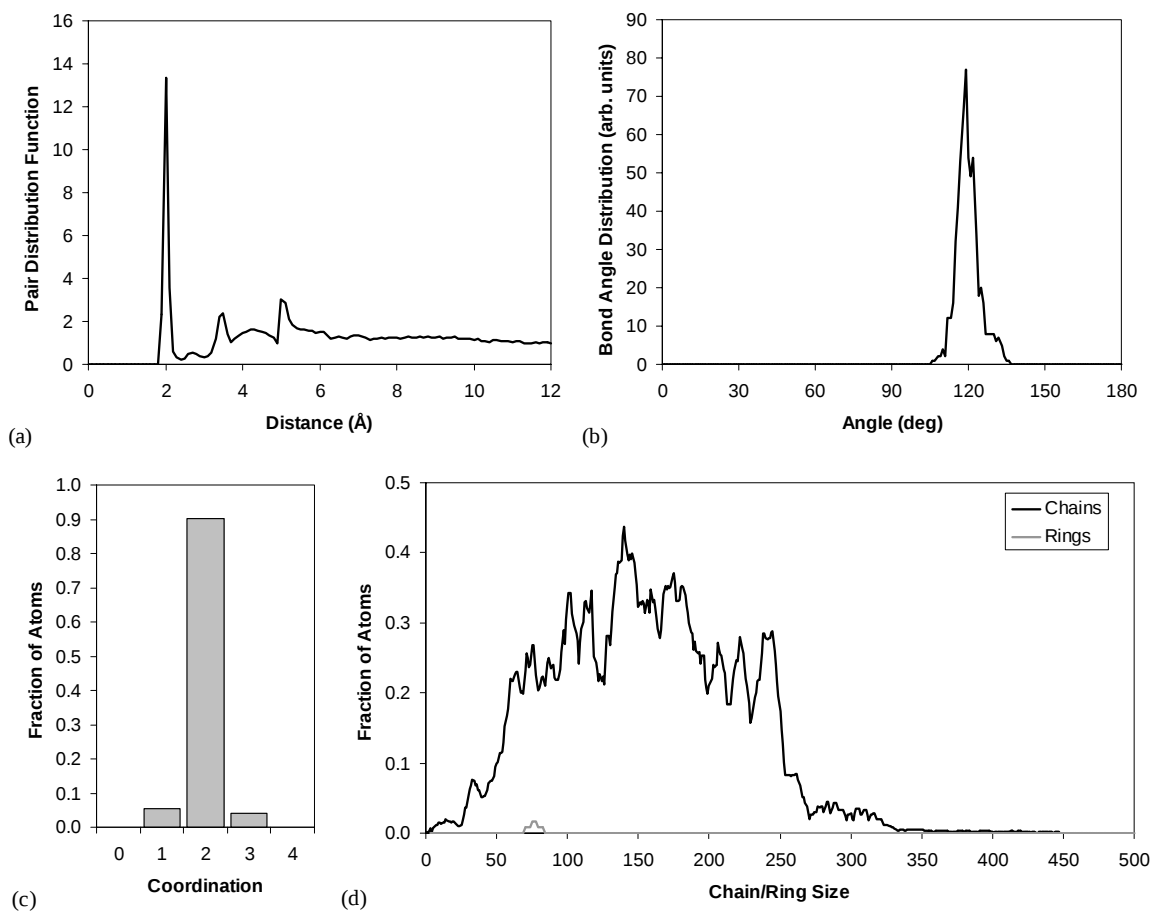


Figure 5.7. Calculated structural data for sulfur glass: (a) pair distribution function, (b) bond angle distribution, (c) coordination number distribution, and (d) chain/ring length distribution.

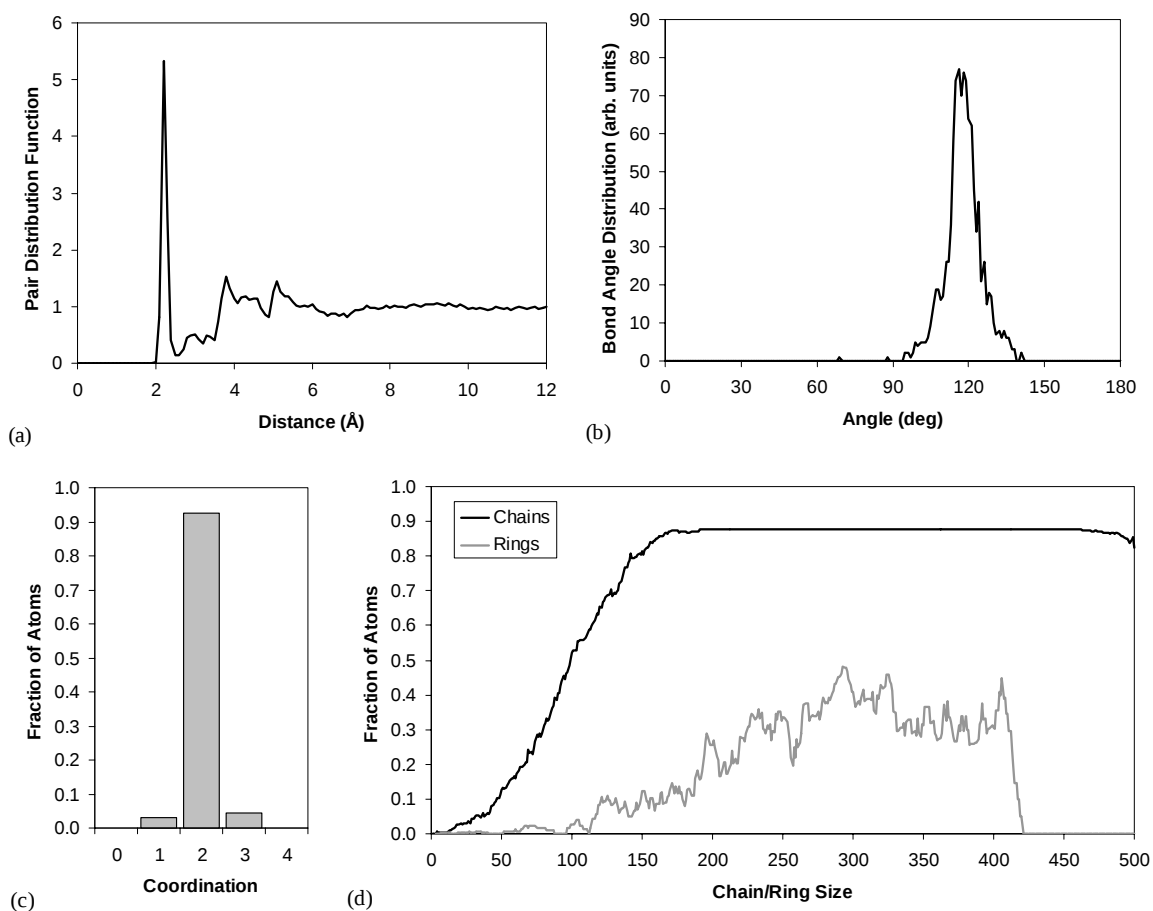


Figure 5.8. Calculated structural data for selenium glass: (a) pair distribution function, (b) bond angle distribution, (c) coordination number distribution, and (d) chain/ring length distribution.

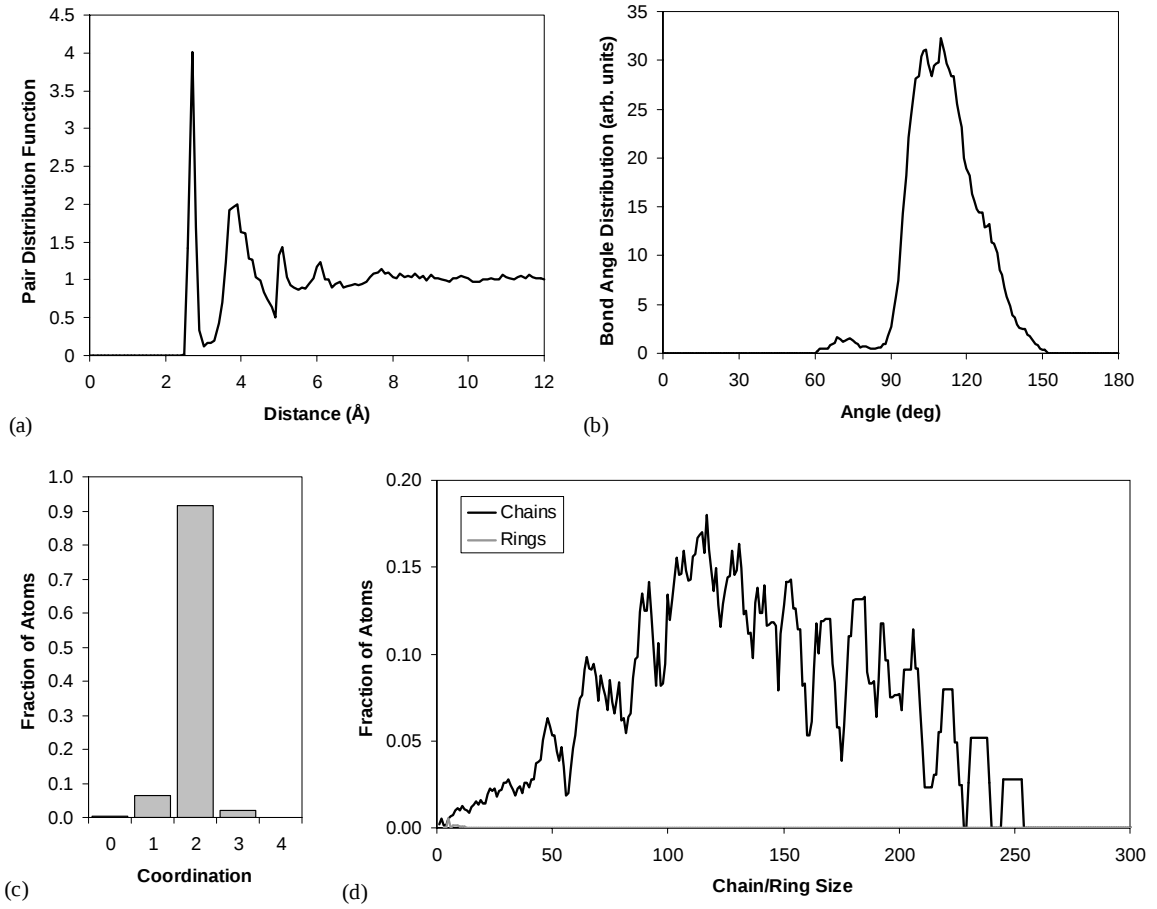


Figure 5.9. Calculated structural data for tellurium glass: (a) pair distribution function, (b) bond angle distribution, (c) coordination number distribution, and (d) chain/ring length distribution.

5.2 $\text{Se}_x\text{Te}_{1-x}$ Glasses

In this section we use the newly developed interaction potentials combined with the Metropolis Monte Carlo molecular simulation technique⁶² to model the structure of glasses in the $\text{Se}_x\text{Te}_{1-x}$ system. The simulations begin by placing 1000 atoms at random positions in a cubic, isochoric simulation space with periodic boundary conditions. The

density of a $\text{Se}_x\text{Te}_{1-x}$ glass is assumed to be $5.9 - 1.6x$ g/cm³, a linear interpolation between the densities of elemental Se and Te, and we consider a constant temperature of $T = 298$ K. We simulate a total of 20 million trial displacements of single atoms with a target acceptance rate of 40%. Plots of the final glass structures for $x = 0.1$ through 0.9 are shown in Figures 5.10-5.19.

Structural data for a $\text{Se}_{0.5}\text{Te}_{0.5}$ glass are provided in Figure 5.20. Whereas the homopolar pair distribution functions in Figure 5.20(a) have strong first-neighbor peaks, the Se-Te pair distribution is zero until after 3 Å and shows very little correlation thereafter. This is a result of the glass's strong preference for homopolar bonding, shown in Figure 5.20(c). Here we see that nearly 99% of all bonds are homopolar, indicating almost perfect phase separation at the covalent chain level. As shown in Figure 5.20(d), the Se and Te atoms are primarily two-coordinated and there is a slightly higher number of mis-coordinated atoms than in the elemental glasses, presumably due to the phase separated nature of the heterogeneous glass. It follows that the chain lengths for $\text{Se}_{0.5}\text{Te}_{0.5}$ glass are shorter than for both elemental glasses, as indicated by Figure 5.20(e). While there is not much experimental data on the $\text{Se}_{0.5}\text{Te}_{0.5}$ system available in literature, our structural data is in good qualitative agreement with the experimental predictions that the glass should consist of two-coordinated chains of atoms¹²³ and is phase separated.¹²⁴

Figure 5.21(a) plots the average coordination number of Se and Te atoms in $\text{Se}_x\text{Te}_{1-x}$ glass as a function of x . We find that the average coordination number of Se drops with low Se content, as does the average coordination number of Te with low Te content. Interestingly, Figure 5.21(b) shows that the fraction of heteropolar bonds increases

with decreasing Se content, indicating that Se is more soluble in a high-Te glass than Te in a high-Se glass. This can also be seen from the glass structure plots in Figures 5.10 through 5.19. Combining these two findings, the average chain length should be a minimum for low Se-content glasses. This result is confirmed by Figure 5.21(c), where we see that the average chain length is a minimum at about $x = 0.2$.

Figure 5.22 compares the distribution of bond types in the $\text{Se}_x\text{Te}_{1-x}$ system versus an ideally mixed homogeneous glass. This figure shows that $\text{Se}_x\text{Te}_{1-x}$ becomes highly phase separated in the regime of $x > 0.2$.

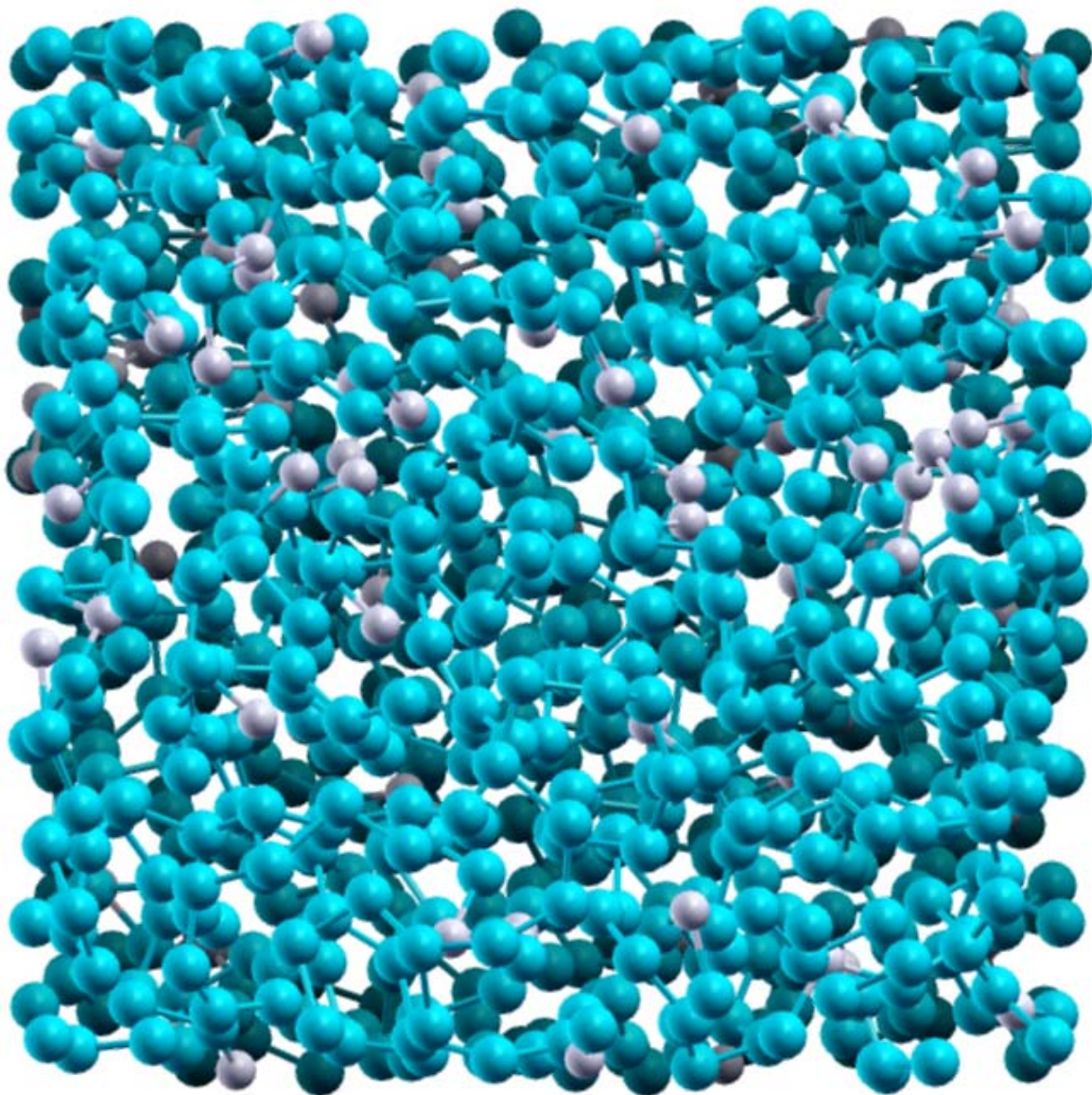


Figure 5.10. Computed structure of $\text{Se}_{0.1}\text{Te}_{0.9}$ glass.

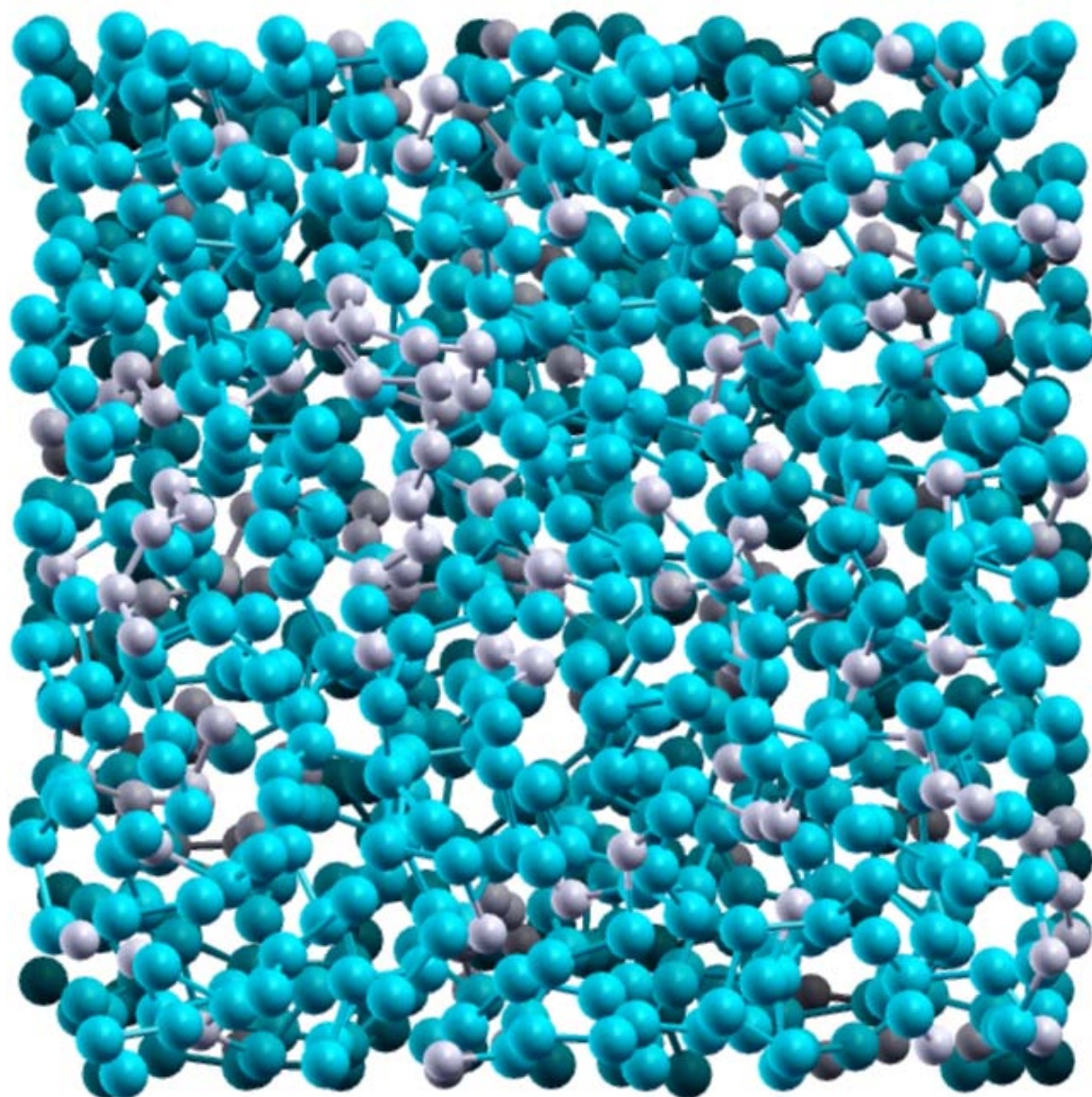


Figure 5.11. Computed structure of $\text{Se}_{0.2}\text{Te}_{0.8}$ glass.

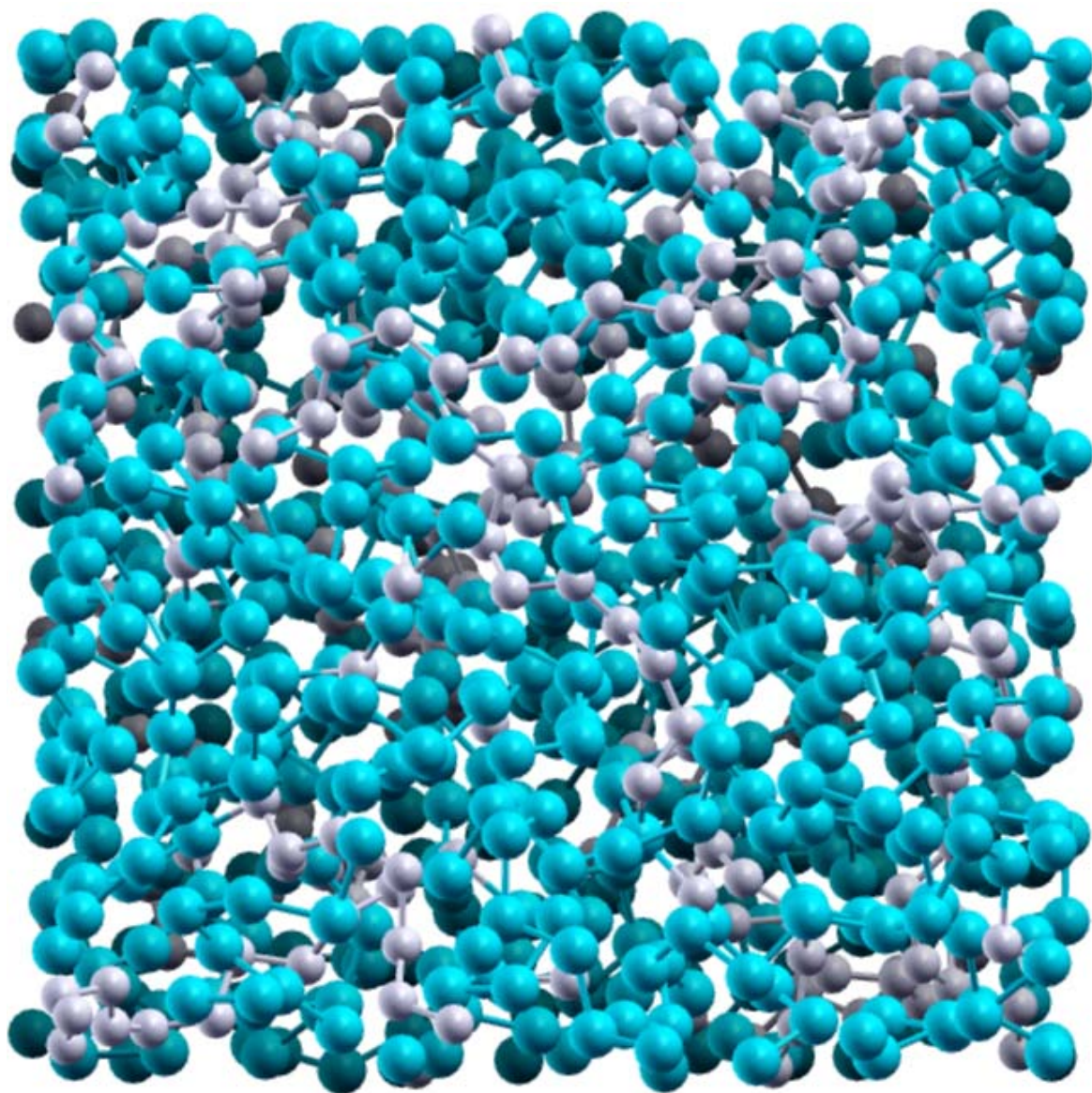


Figure 5.12. Computed structure of $\text{Se}_{0.3}\text{Te}_{0.7}$ glass.

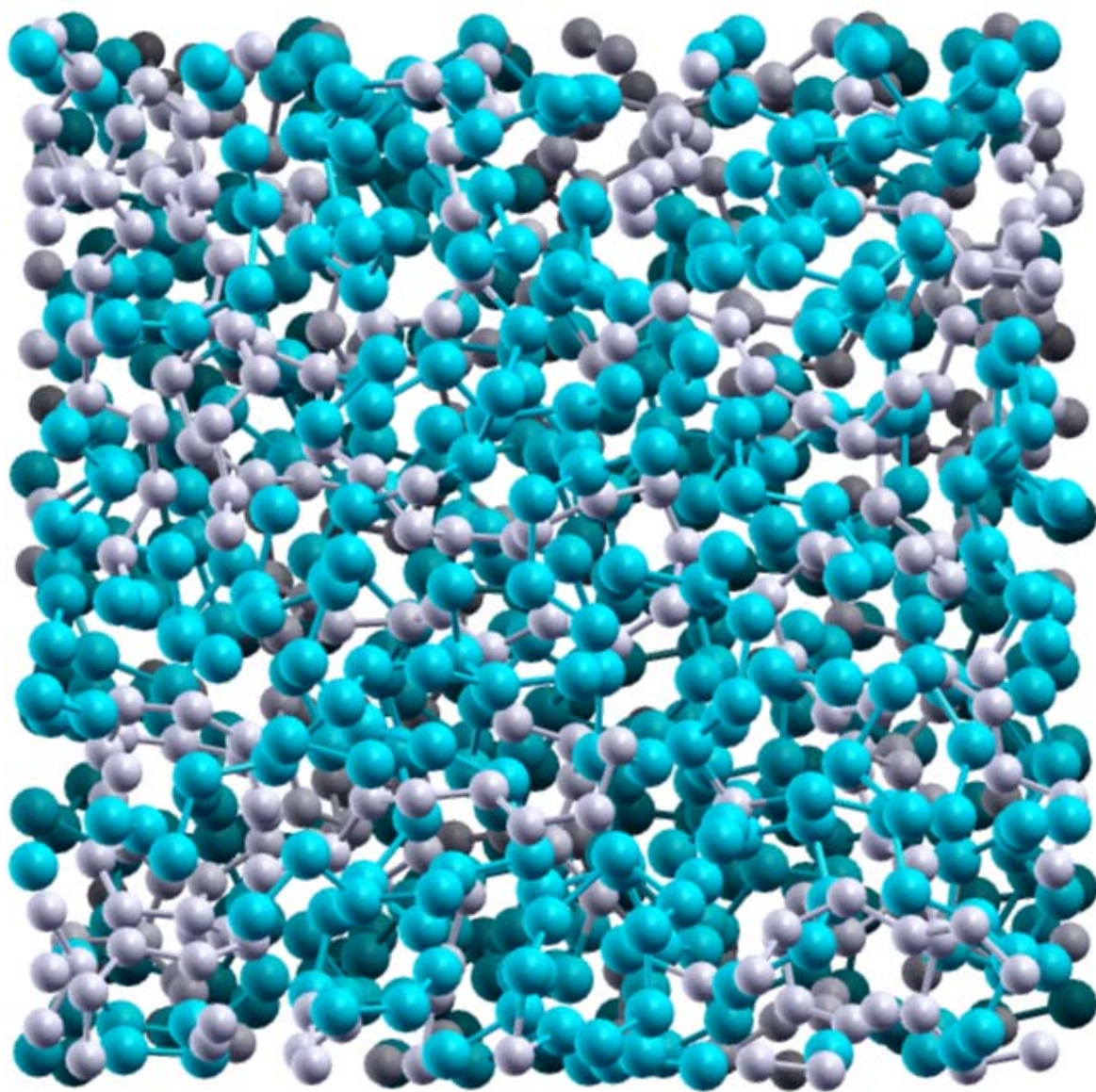


Figure 5.13. Computed structure of $\text{Se}_{0.4}\text{Te}_{0.6}$ glass.

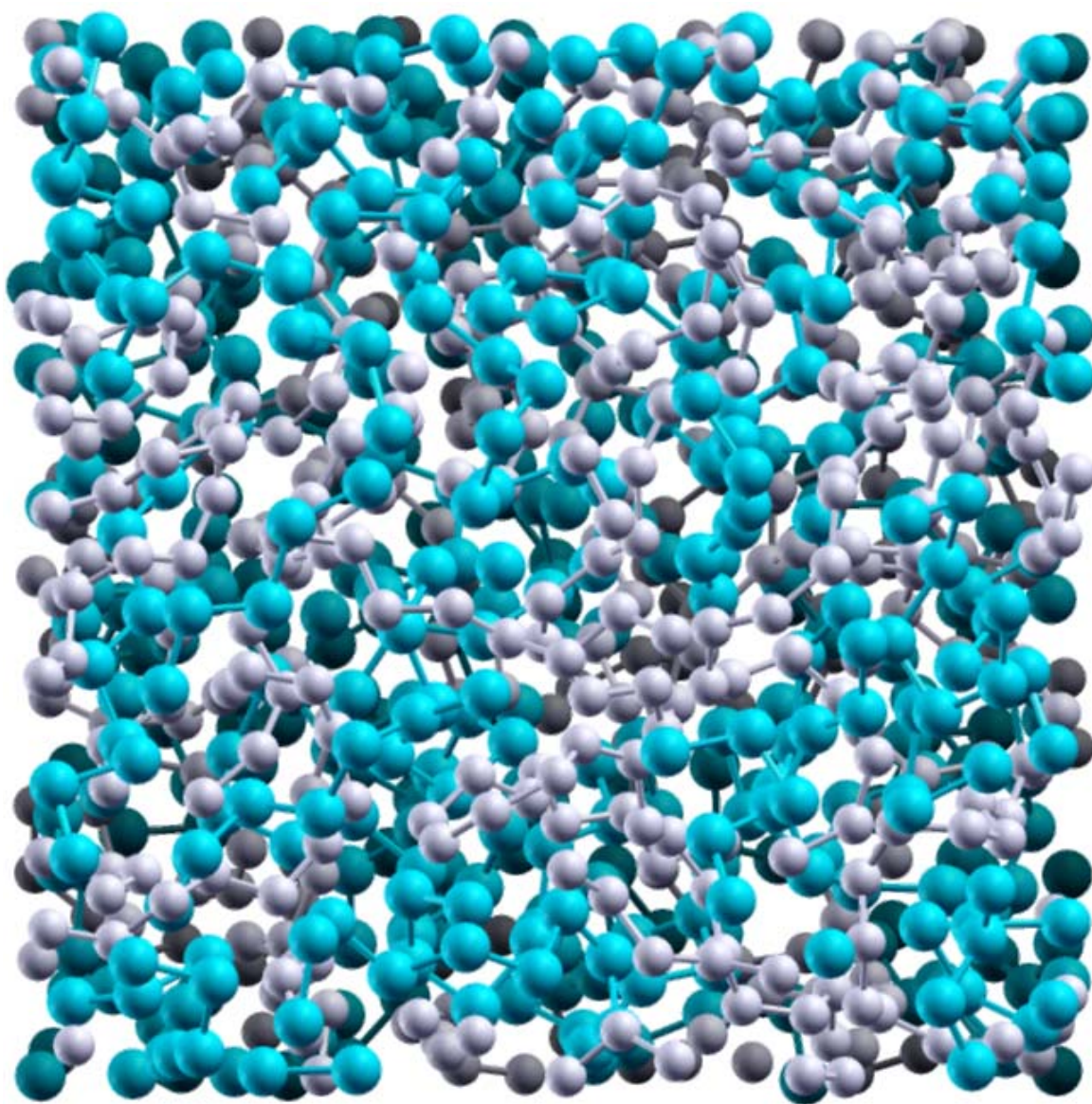


Figure 5.14. Computed structure of $\text{Se}_{0.5}\text{Te}_{0.5}$ glass.

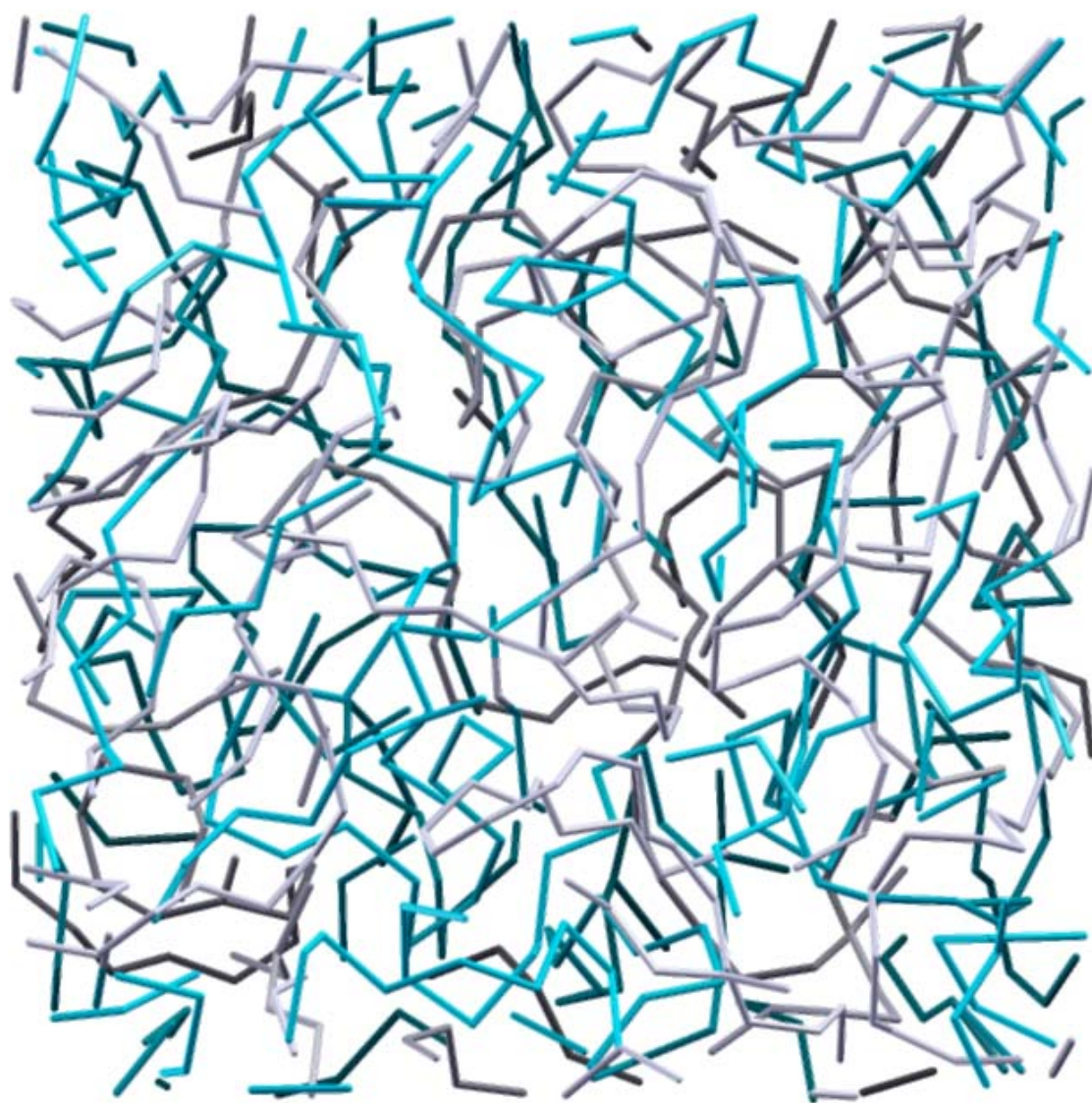


Figure 5.15. Computed structure of $\text{Se}_{0.5}\text{Te}_{0.5}$ glass (stick representation).

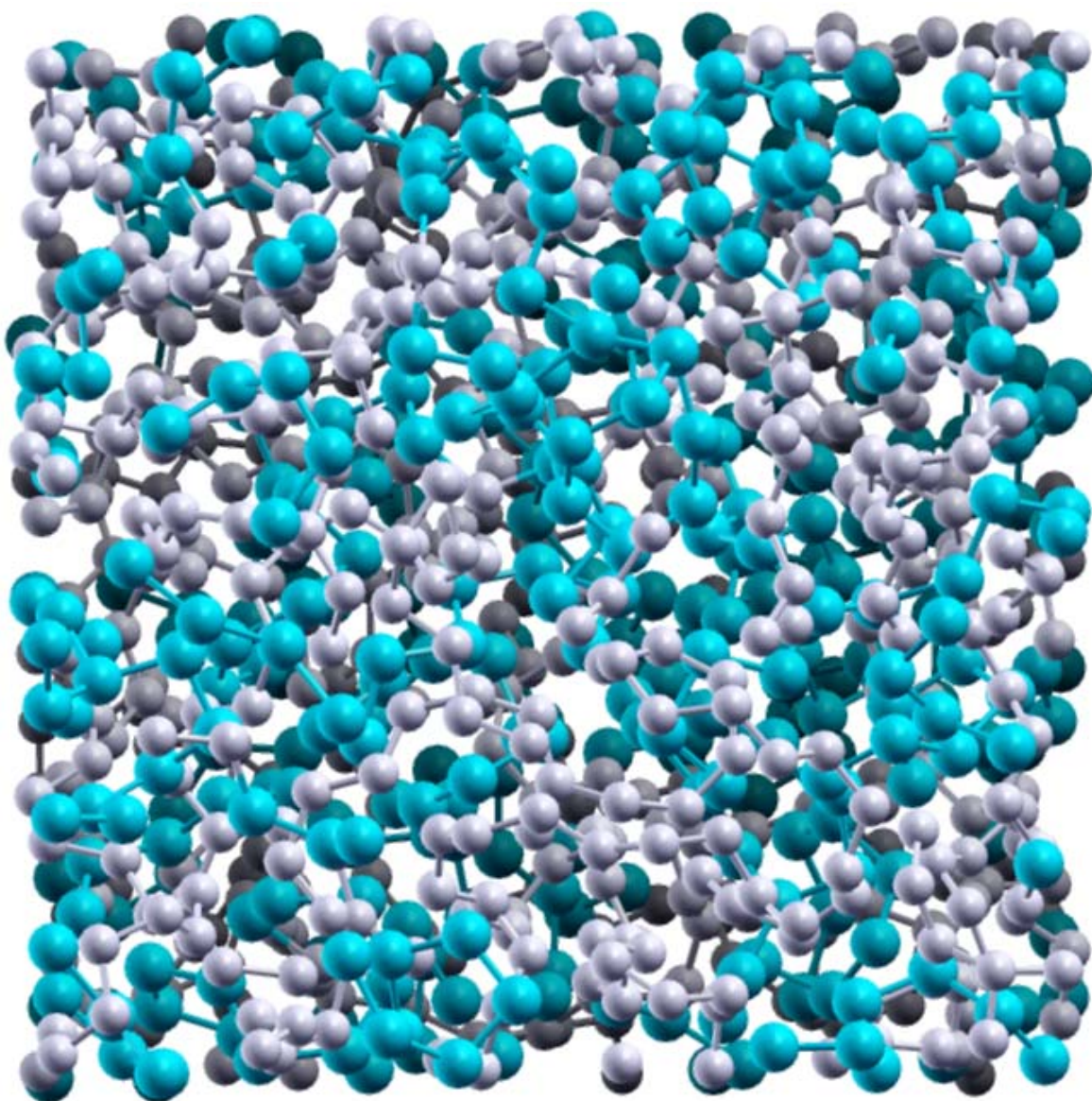


Figure 5.16. Computed structure of $\text{Se}_{0.6}\text{Te}_{0.4}$ glass.

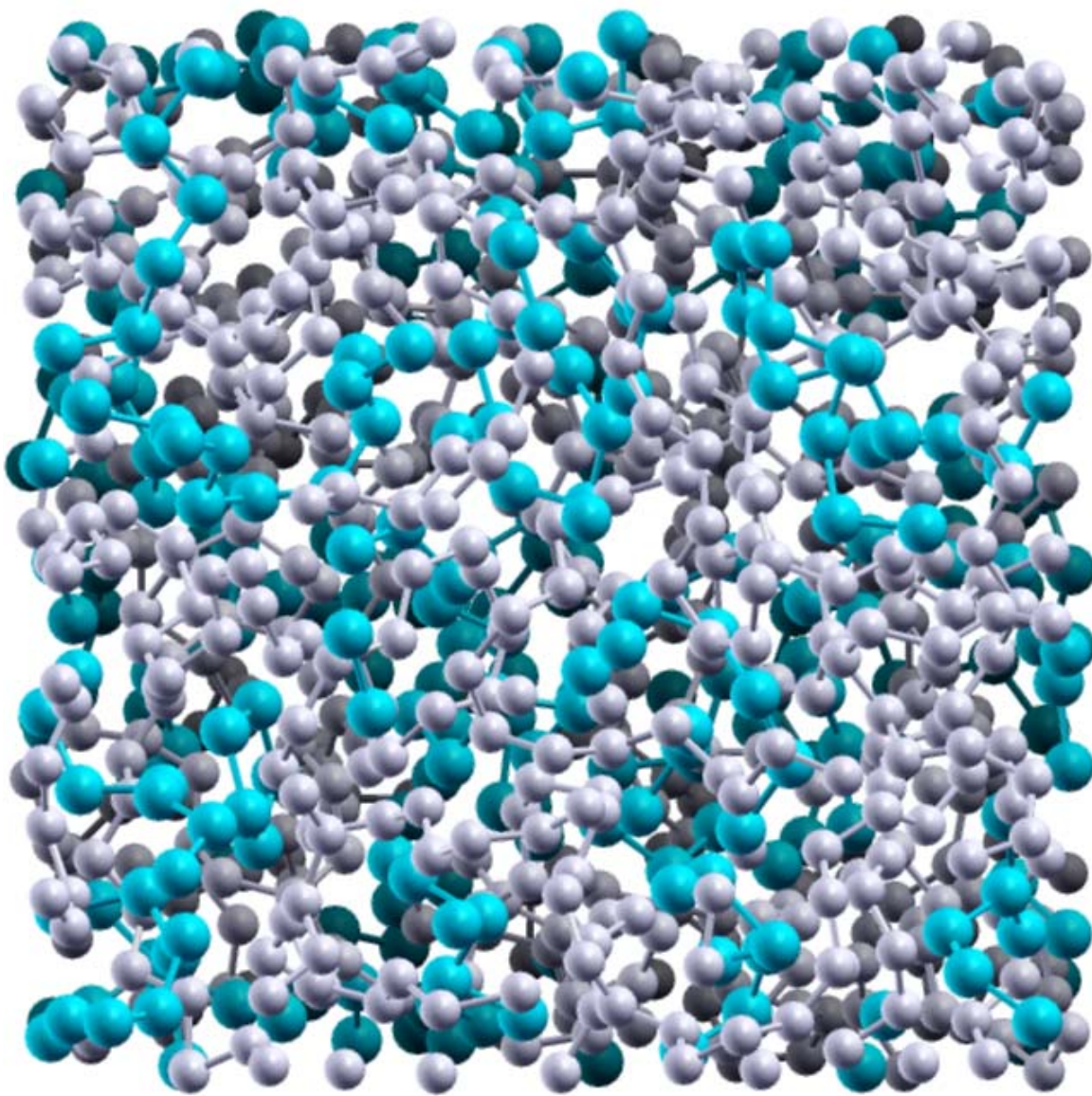


Figure 5.17. Computed structure of $\text{Se}_{0.7}\text{Te}_{0.3}$ glass.

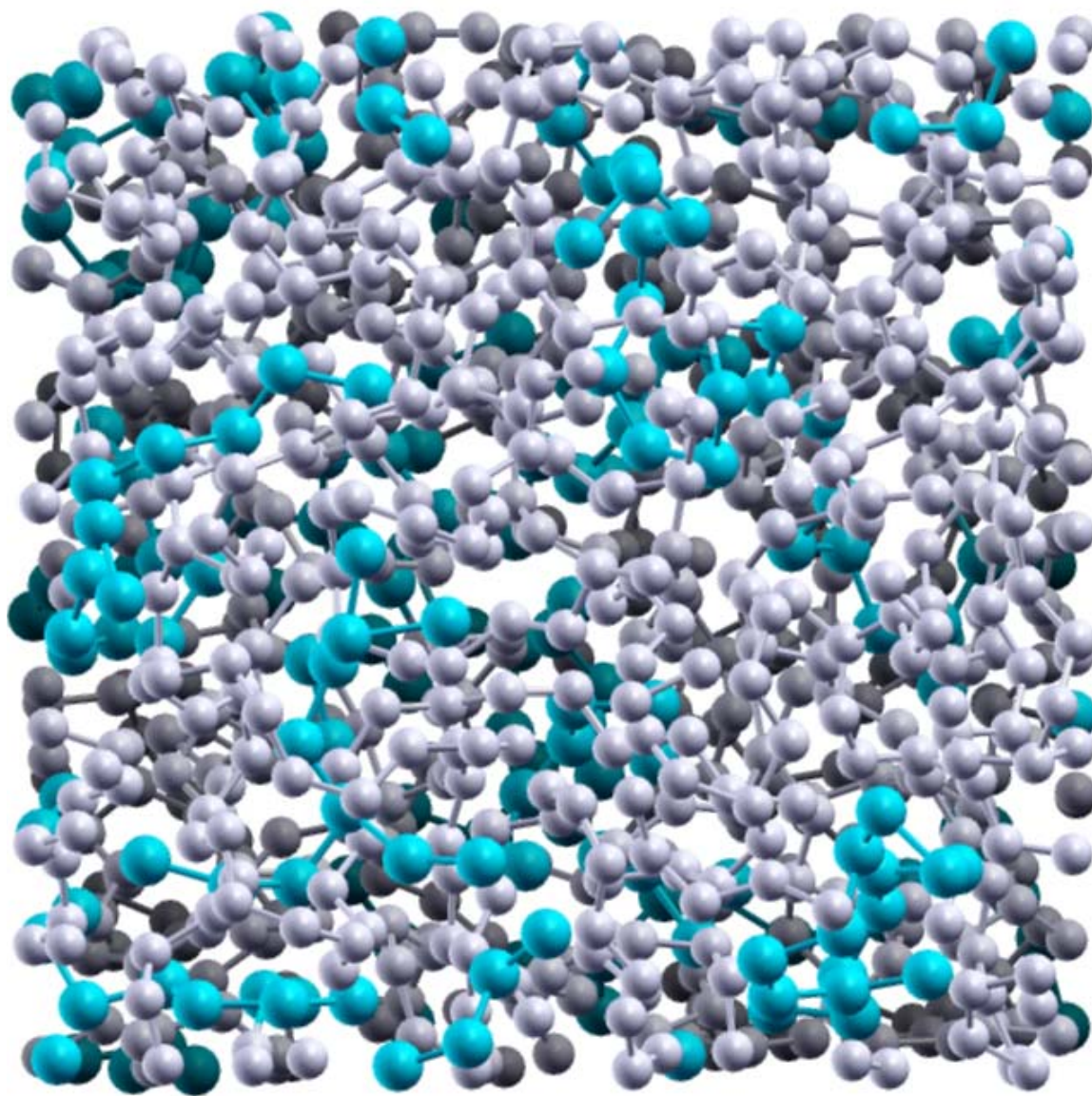


Figure 5.18. Computed structure of $\text{Se}_{0.8}\text{Te}_{0.2}$ glass.

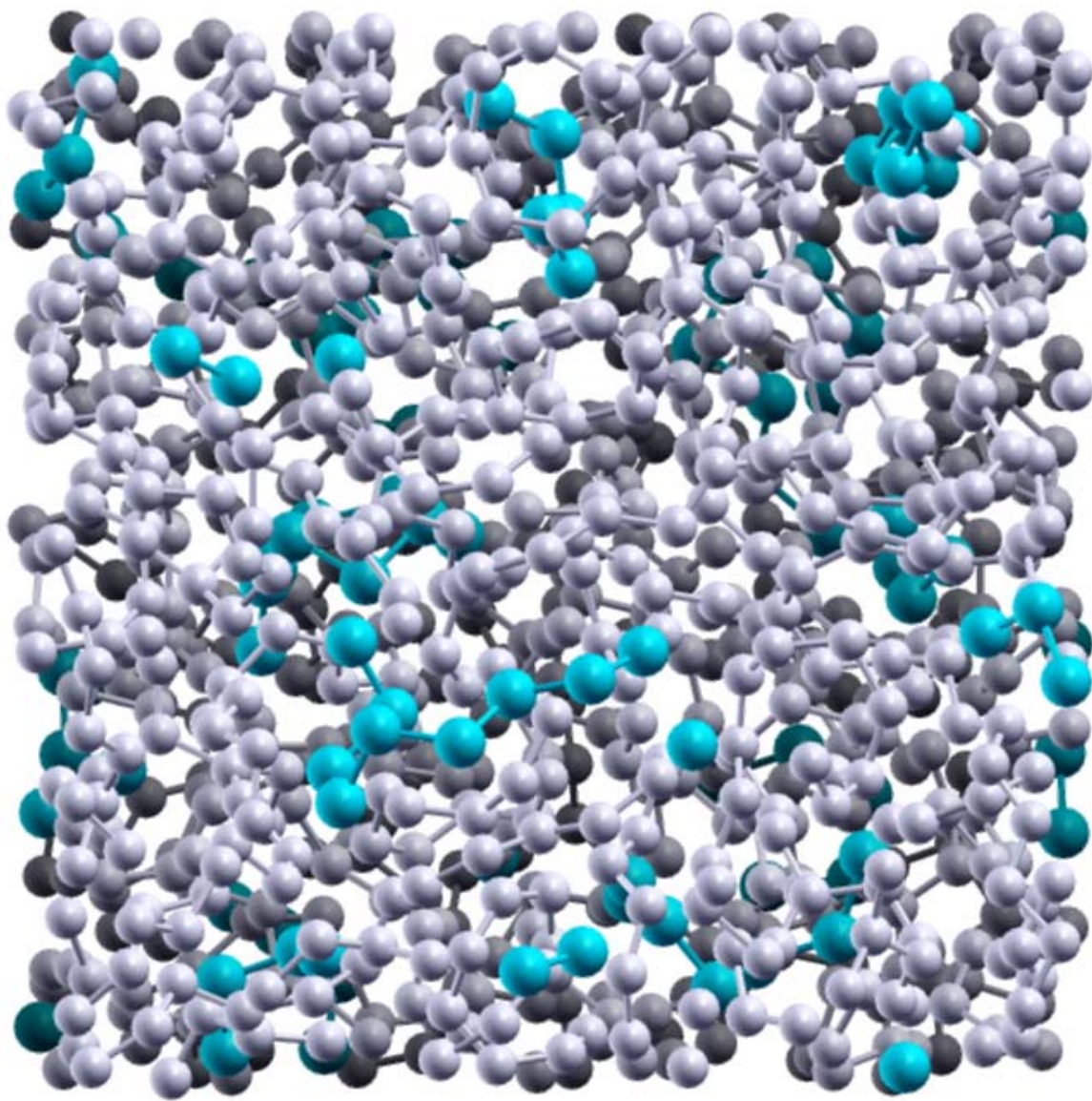


Figure 5.19. Computed structure of $\text{Se}_{0.9}\text{Te}_{0.1}$ glass.

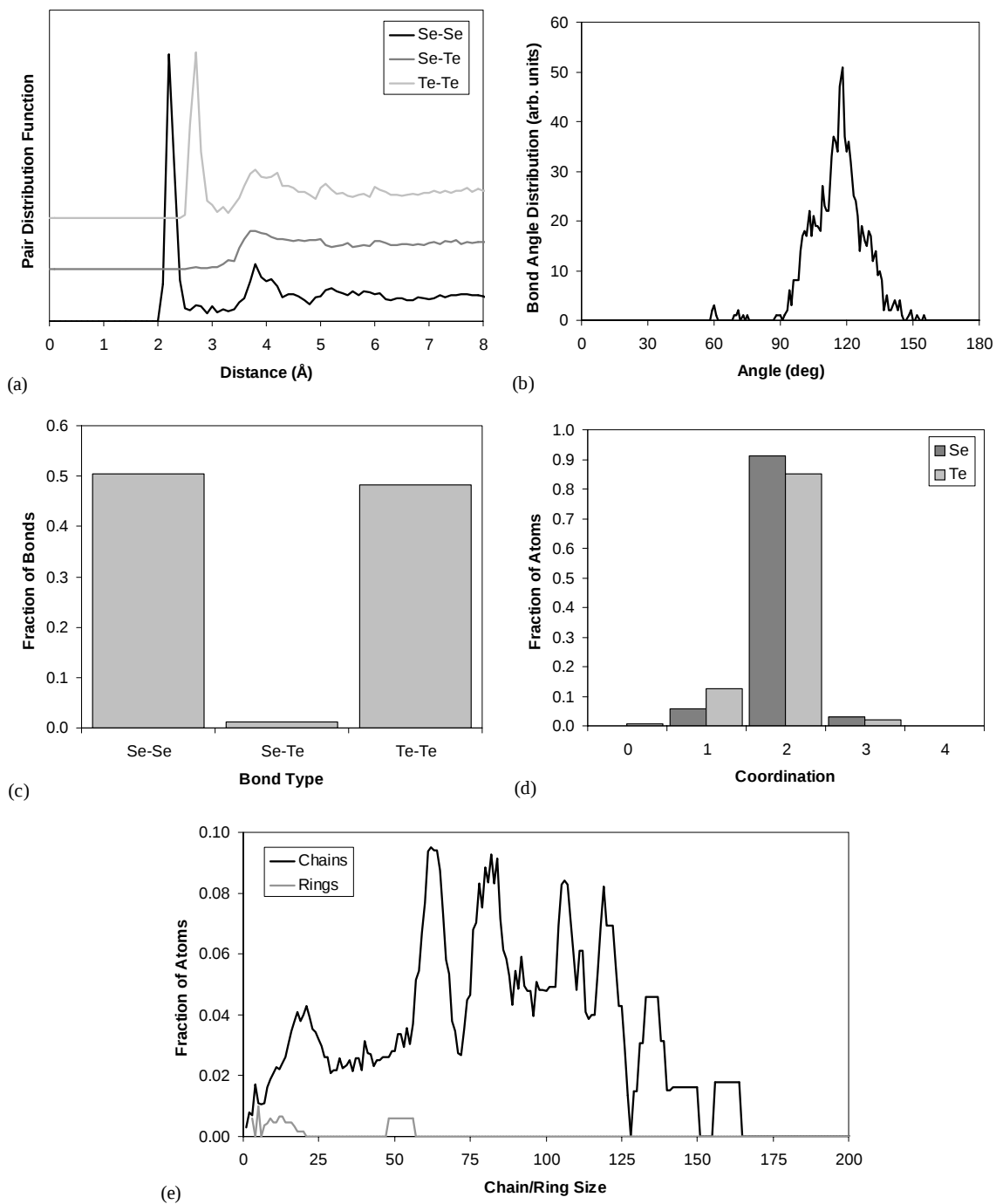


Figure 5.20. Calculated structural data for $\text{Se}_{0.5}\text{Te}_{0.5}$ glass: (a) pair distribution functions, (b) bond angle distribution, (c) bond population, (d) coordination number distribution, and (e) chain/ring length distributions.

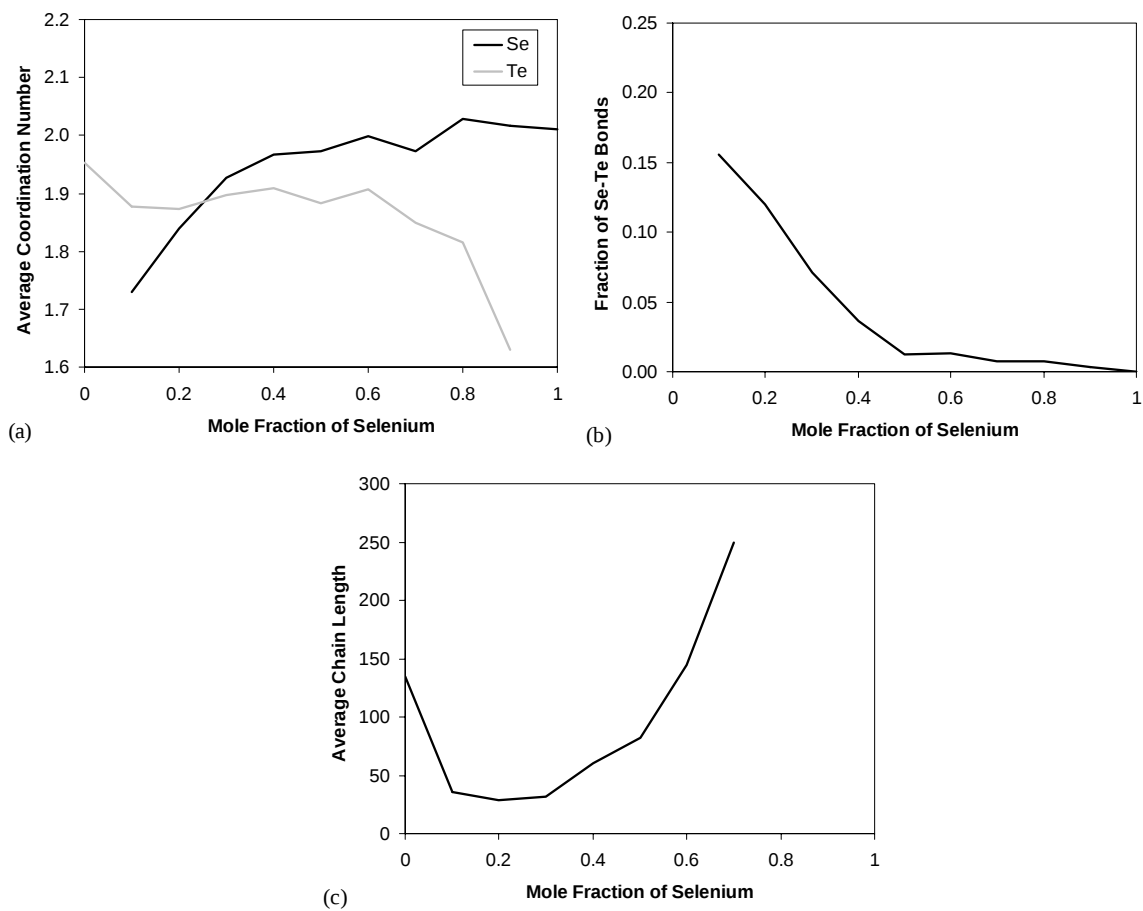


Figure 5.21. Calculated structural data for glasses in the $\text{Se}_x\text{Te}_{1-x}$ system: (a) average coordination number, (b) fraction of heteropolar bonds, and (c) average chain length.

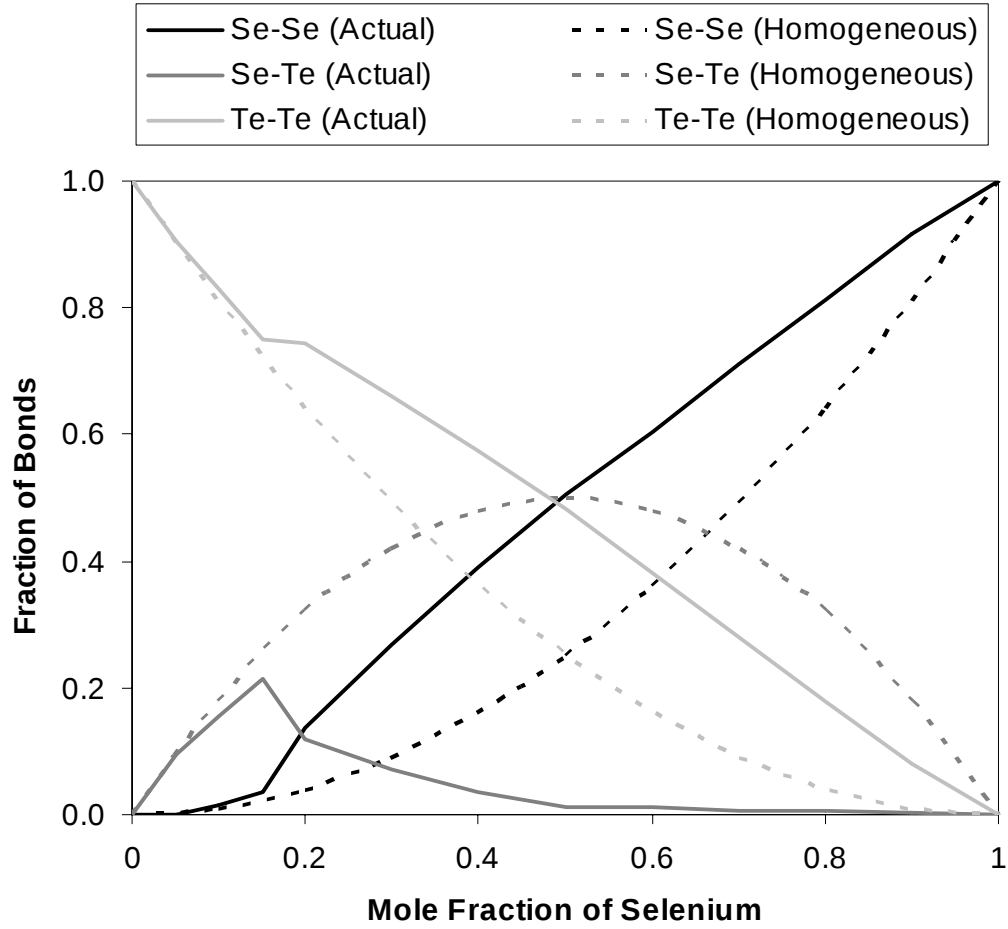


Figure 5.22. Distribution of bond types for glasses in the $\text{Se}_x\text{Te}_{1-x}$ system (solid lines) compared to that of a perfectly homogeneous glass (dashed lines).

5.3 $\text{S}_x\text{Se}_{1-x}$ Glasses

We compute the structures of glasses in the binary $\text{S}_x\text{Se}_{1-x}$ following the same procedure as for the elemental glasses in Section 5.1. The density of a $\text{S}_x\text{Se}_{1-x}$ glass is assumed to be $4.30 - 2.55x \text{ g/cm}^3$, a linear interpolation between the densities of elemental S and Se, and we consider a constant temperature of $T = 200 \text{ K}$. Plots of the final glass

structures are shown in Figures 5.23-5.32 for $x = 0.1$ through 0.9.

Figure 5.28 shows that $S_{0.5}Se_{0.5}$ glass consists of many kinked, tangled chains of atoms. The S-S, S-Se, and Se-Se pair distribution functions for this glass are given in Figure 5.33(a), where we can see that the nearest-neighbor distances are well-defined for all three cases. This is in contrast to our previous modeling of $Se_{0.5}Te_{0.5}$ glass, in which a nearest-neighbor peak for the Se-Te pair distribution was not observed. Whereas $Se_{0.5}Te_{0.5}$ glass is composed almost exclusively of segregated chains of selenium and tellurium atoms with little Se-Te bonding, Figure 5.33(c) shows that $S_{0.5}Se_{0.5}$ exhibits significant heteropolar and homopolar bonding. This leads to the well-defined first-neighbor peaks shown in Figure 5.33(a).

The second- and third-nearest neighbor positions in Figure 5.33(a) are more diffuse owing to the bond angle distribution shown in Figure 5.33(b). The bond angle distribution is centered around 118° and ranges from 96° to 143° . This is very similar to the bond angle distributions we obtained previously for elemental sulfur and selenium glasses. Figure 5.33(a) shows that the glassy structure becomes completely disordered after about 7 Å.

The distributions of atomic coordination numbers for sulfur and selenium atoms in $S_{0.5}Se_{0.5}$ glass are plotted in Figure 5.33(d). Here we see that about 85% of S and Se atoms are two-coordinated, giving a “defect” rate of about 15%. Most defective atoms are either one- and three-coordinated, with sulfur atoms exhibiting a greater tendency for the higher coordination. The average coordination numbers for sulfur and selenium in $S_{0.5}Se_{0.5}$ glass are 2.07 and 1.94, respectively, where the bond cutoffs are taken to be the first zeroes in the pair distribution functions (2.4, 2.5, and 2.6 Å for S-S, S-Se, and Se-Se, respectively).

Figure 5.33(e) plots the fraction of atoms that are members of chains or rings of different sizes. Three-coordinated atoms lead to branching that allows a single atom to be a member of multiple chains and rings simultaneously. Figure 5.33(e) shows that the structure of $S_{0.5}Se_{0.5}$ glass is dominated by long chains and, to a lesser extent, by large rings composed of about 60-400 atoms. This is a similar result as obtained for elemental selenium glass, but with a somewhat larger presence of rings. The average chain length for $S_{0.5}Se_{0.5}$ is 268 atoms. Very few rings were found in our previous study of $Se_{0.5}Te_{0.5}$ glass, and the average chain length for that case was only 83 atoms.

Figures 5.34 and 5.35 plot structural results for glasses in the S_xSe_{1-x} system for varying sulfur content, x . Figure 5.34 shows the distribution of bond types in the simulated S_xSe_{1-x} system versus an ideally homogeneous case. There is some preference for homopolar bonding in the region of $x < 0.7$. High sulfur-content glasses are nearly homogeneous. Figure 5.35 shows that the average chain length decreases at high mole fractions of sulfur. The average chain length of S glass is just over half that of Se glass. This decrease in chain length is due to a slightly higher defect concentration in sulfur.

Unfortunately there is very little data in literature with which to validate our model of S_xSe_{1-x} glass. Our model of the binary S_xSe_{1-x} system is the first of its kind, and there has been very little experimental work on this system. Fukunaga *et al.*¹²⁵ prepared amorphous $S_{0.5}Se_{0.5}$ through mechanical alloying, i.e., milling of sulfur and selenium powders for tens of hours. However, this method failed to produce a material that was truly amorphous at atomic scales.¹²⁵

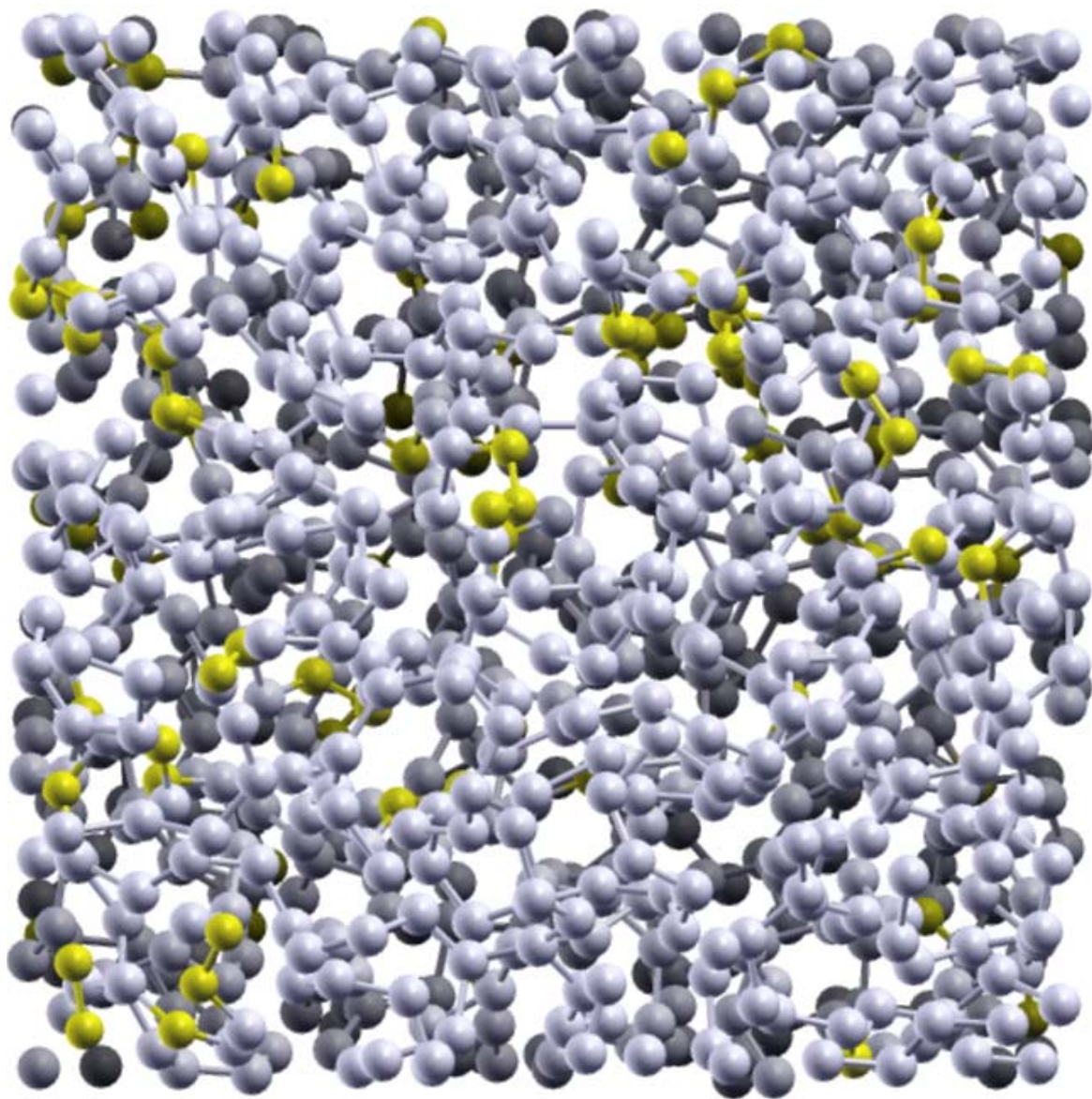


Figure 5.23. Computed structure of $S_{0.1}Se_{0.9}$ glass.

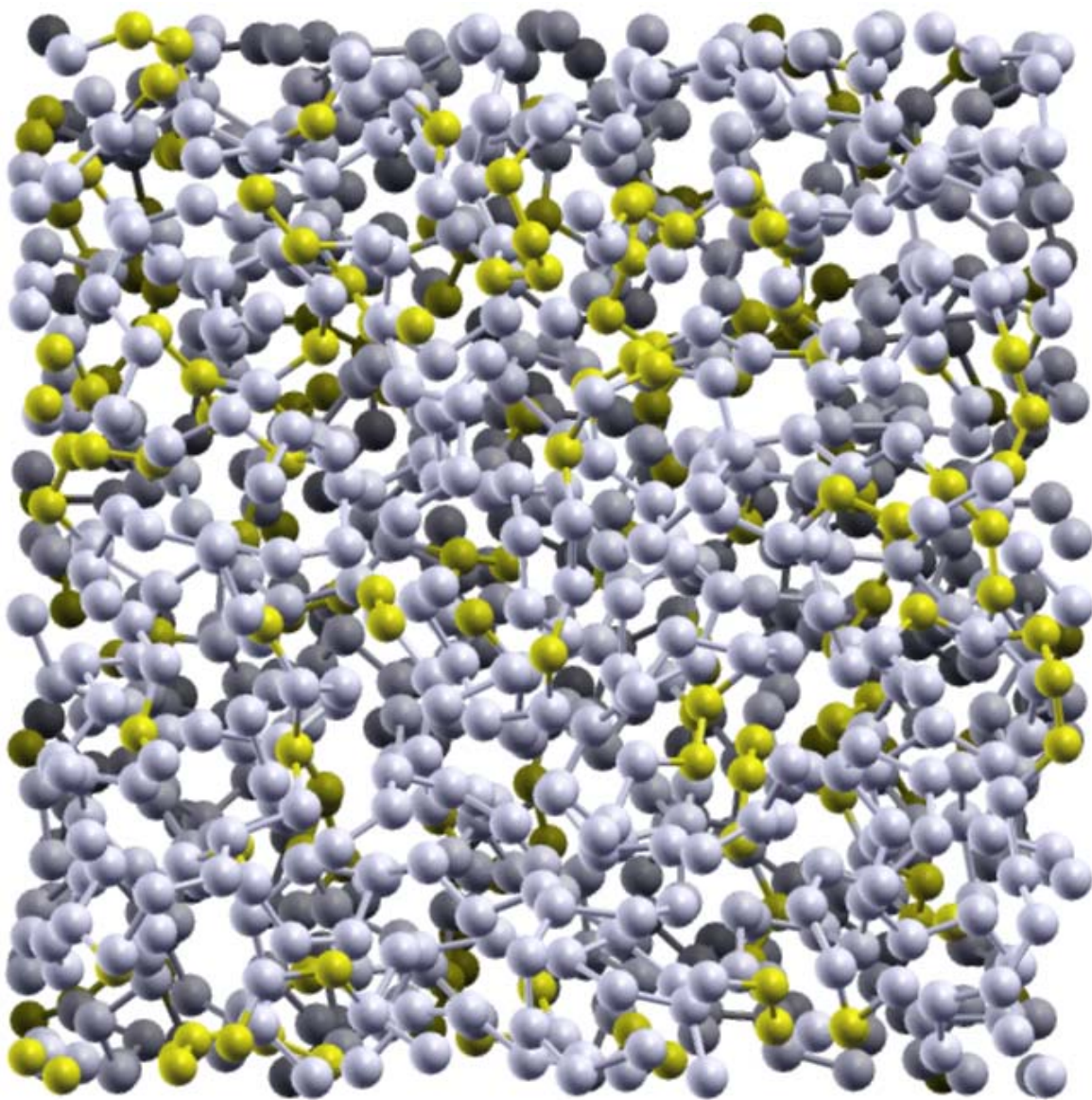


Figure 5.24. Computed structure of $S_{0.2}Se_{0.8}$ glass.

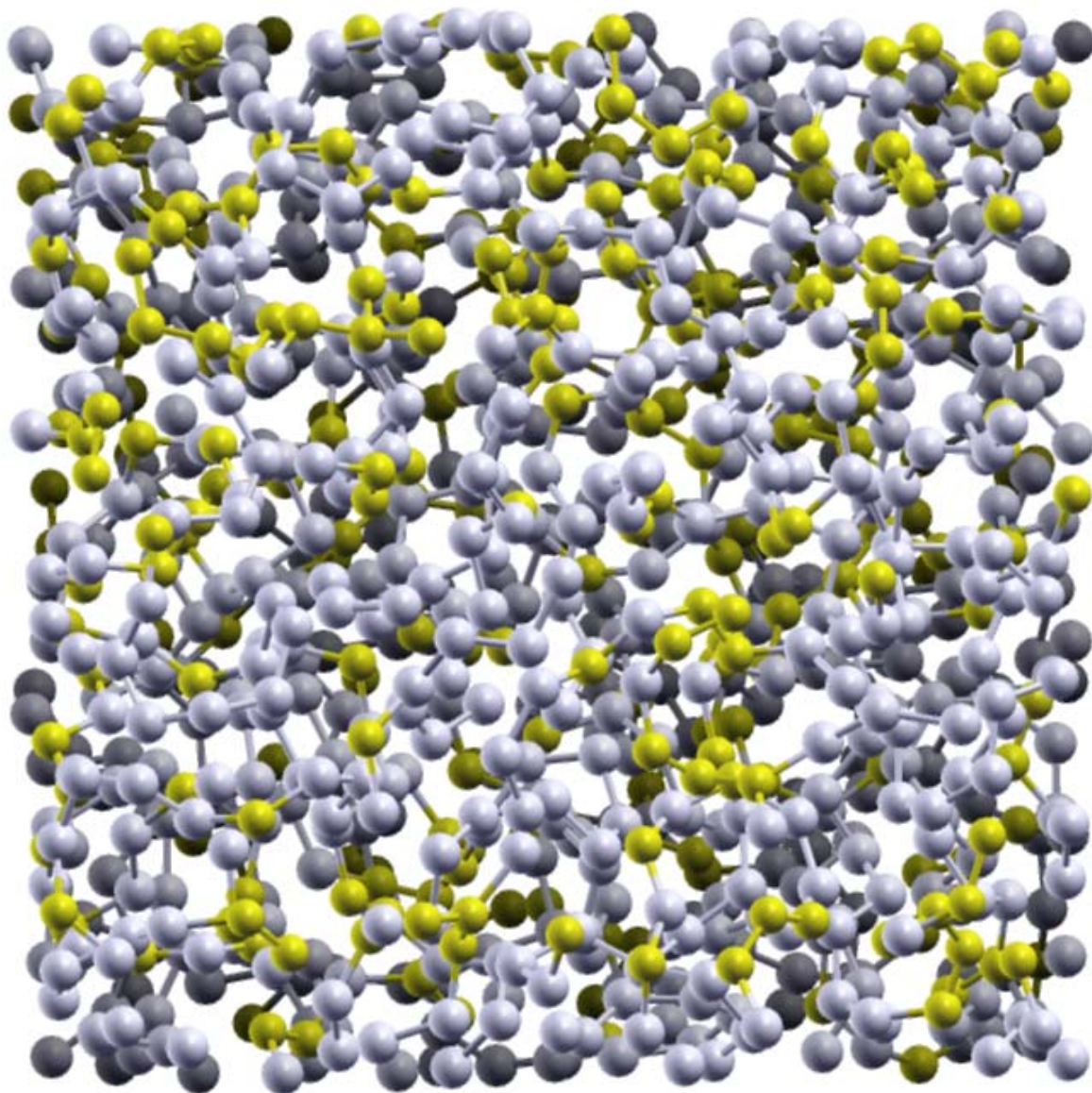


Figure 5.25. Computed structure of $S_{0.3}Se_{0.7}$ glass.

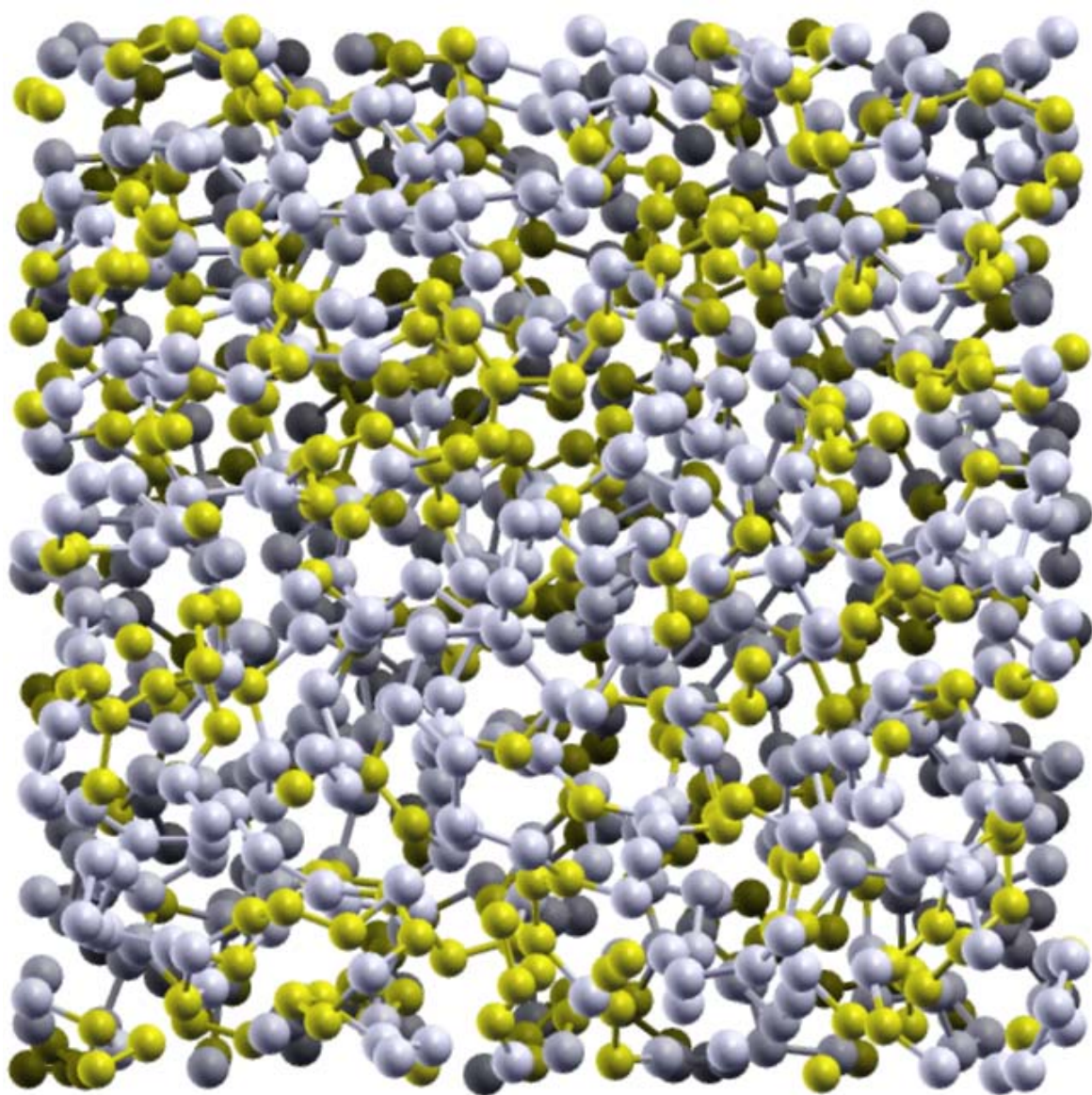


Figure 5.26. Computed structure of $S_{0.4}Se_{0.6}$ glass.

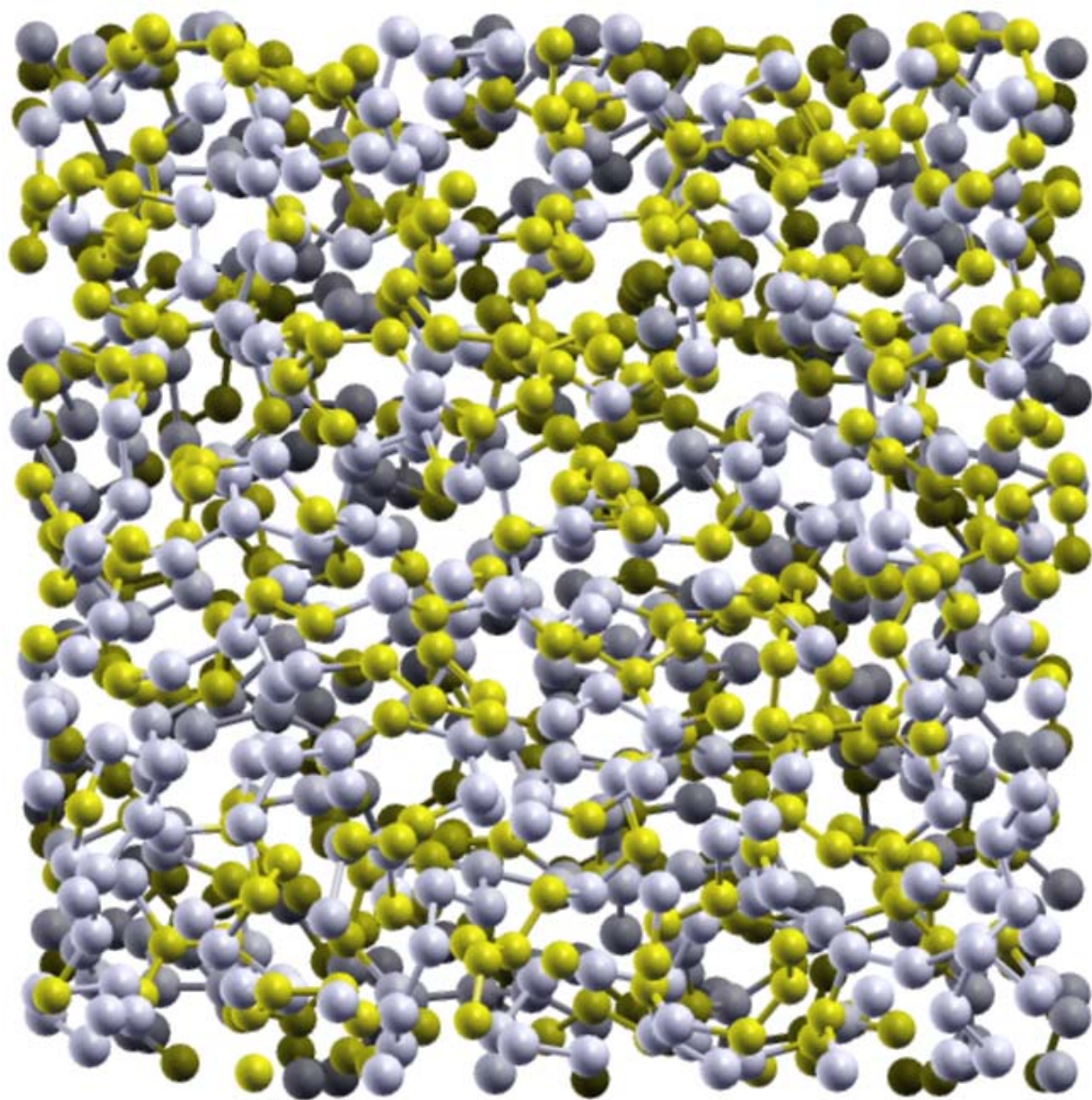


Figure 5.27. Computed structure of $S_{0.5}Se_{0.5}$ glass.

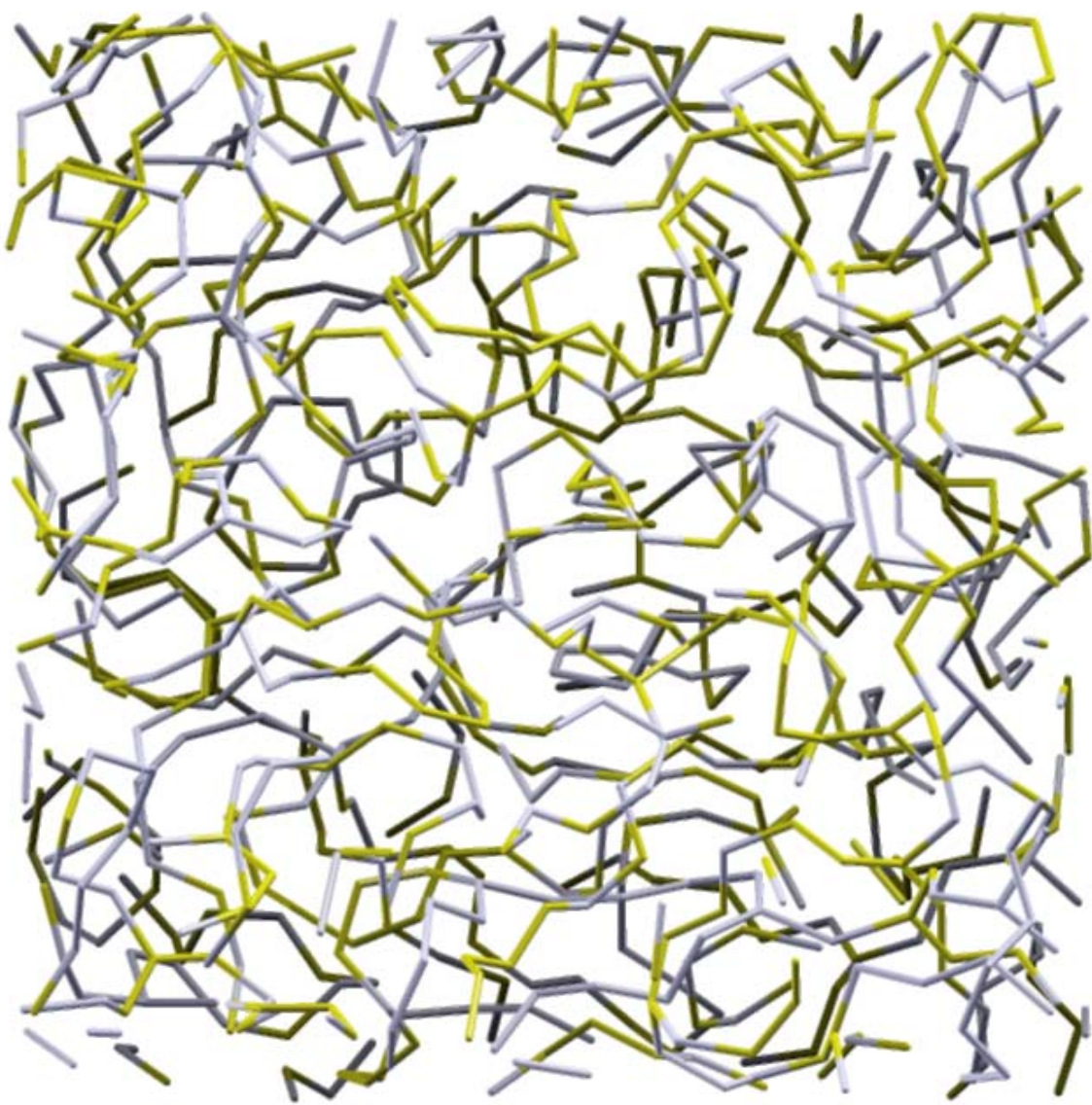


Figure 5.28. Computed structure of $S_{0.5}Se_{0.5}$ glass (stick representation).

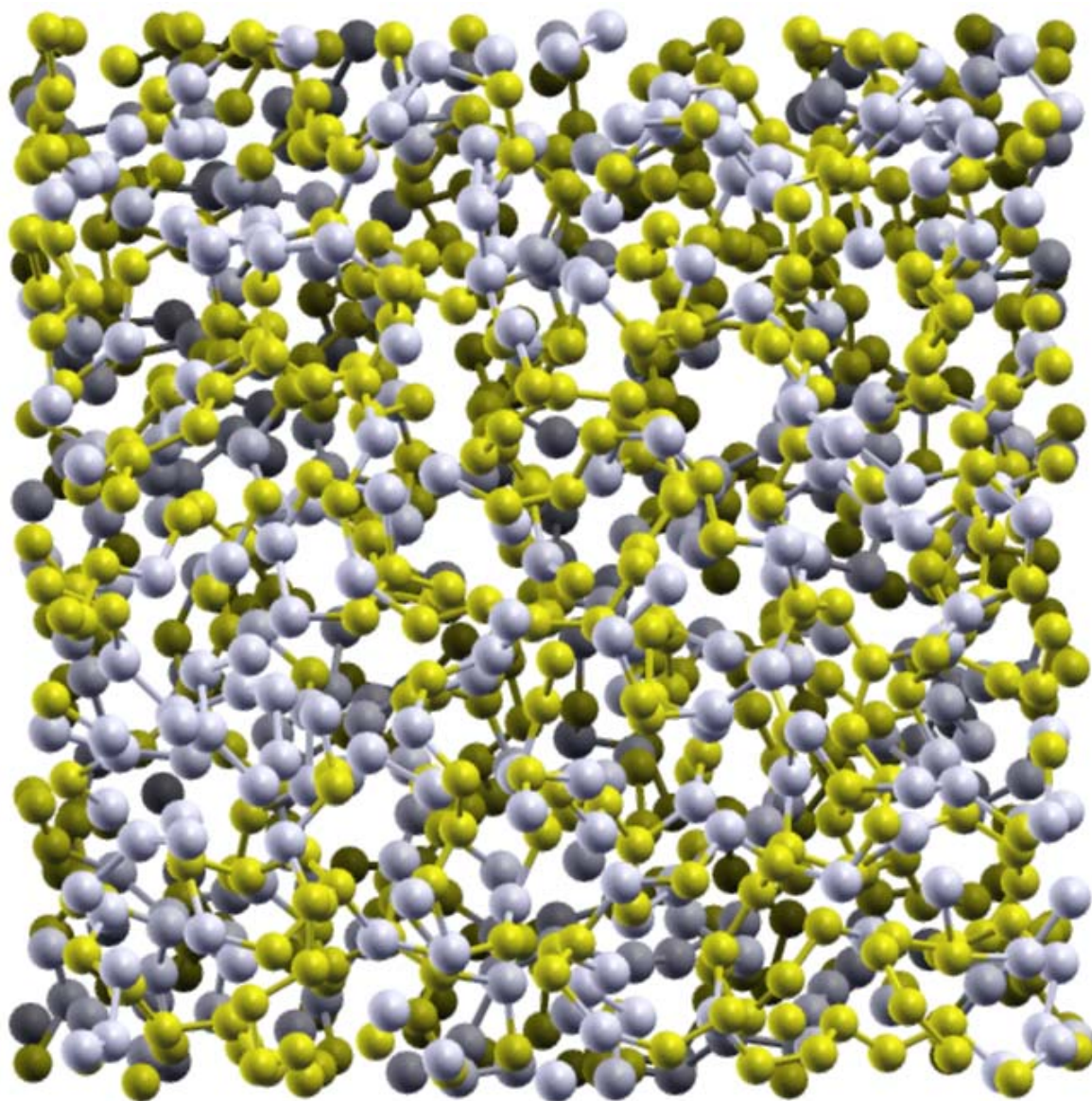


Figure 5.29. Computed structure of $S_{0.6}Se_{0.4}$ glass.

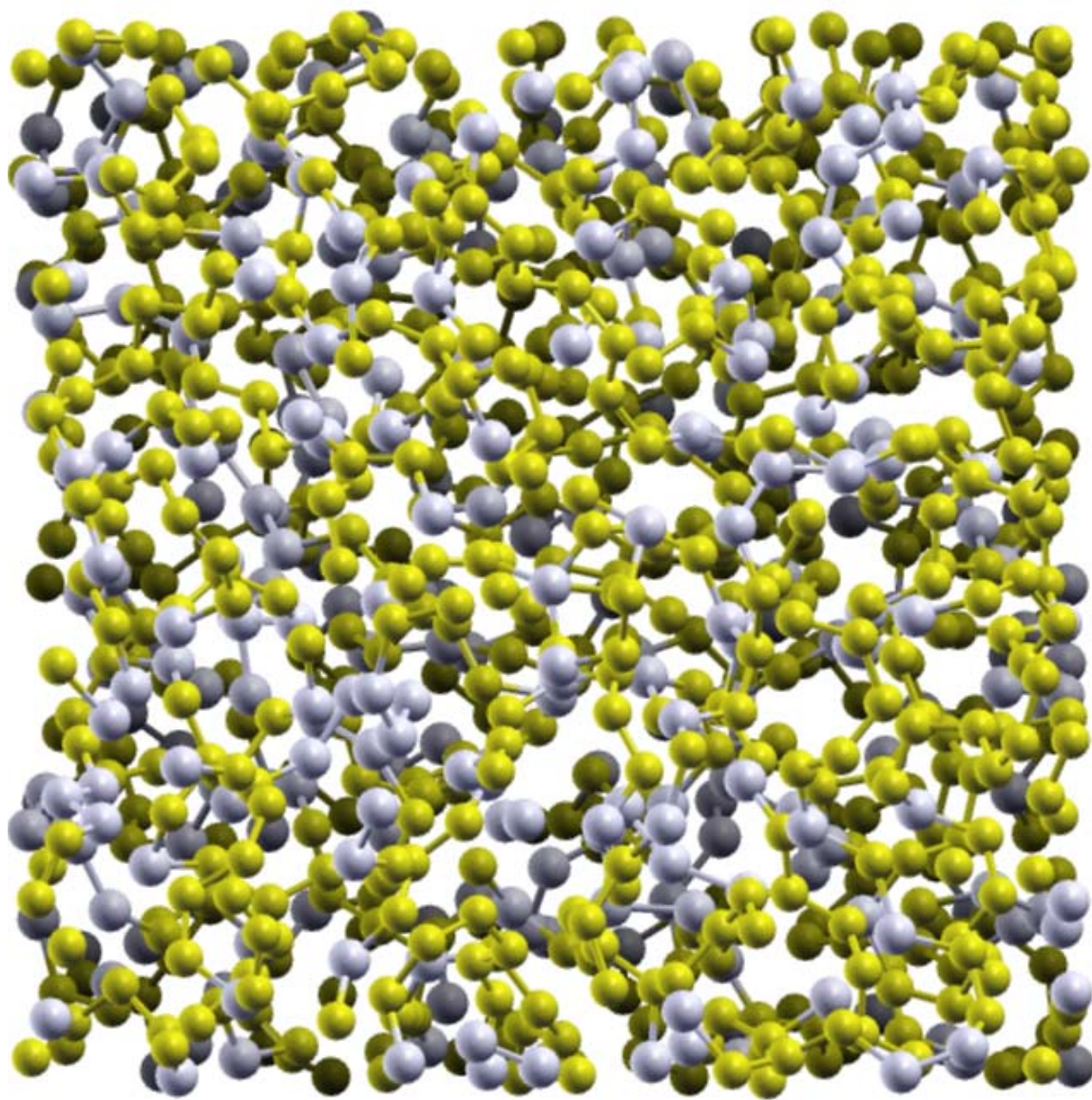


Figure 5.30. Computed structure of $S_{0.7}Se_{0.3}$ glass.

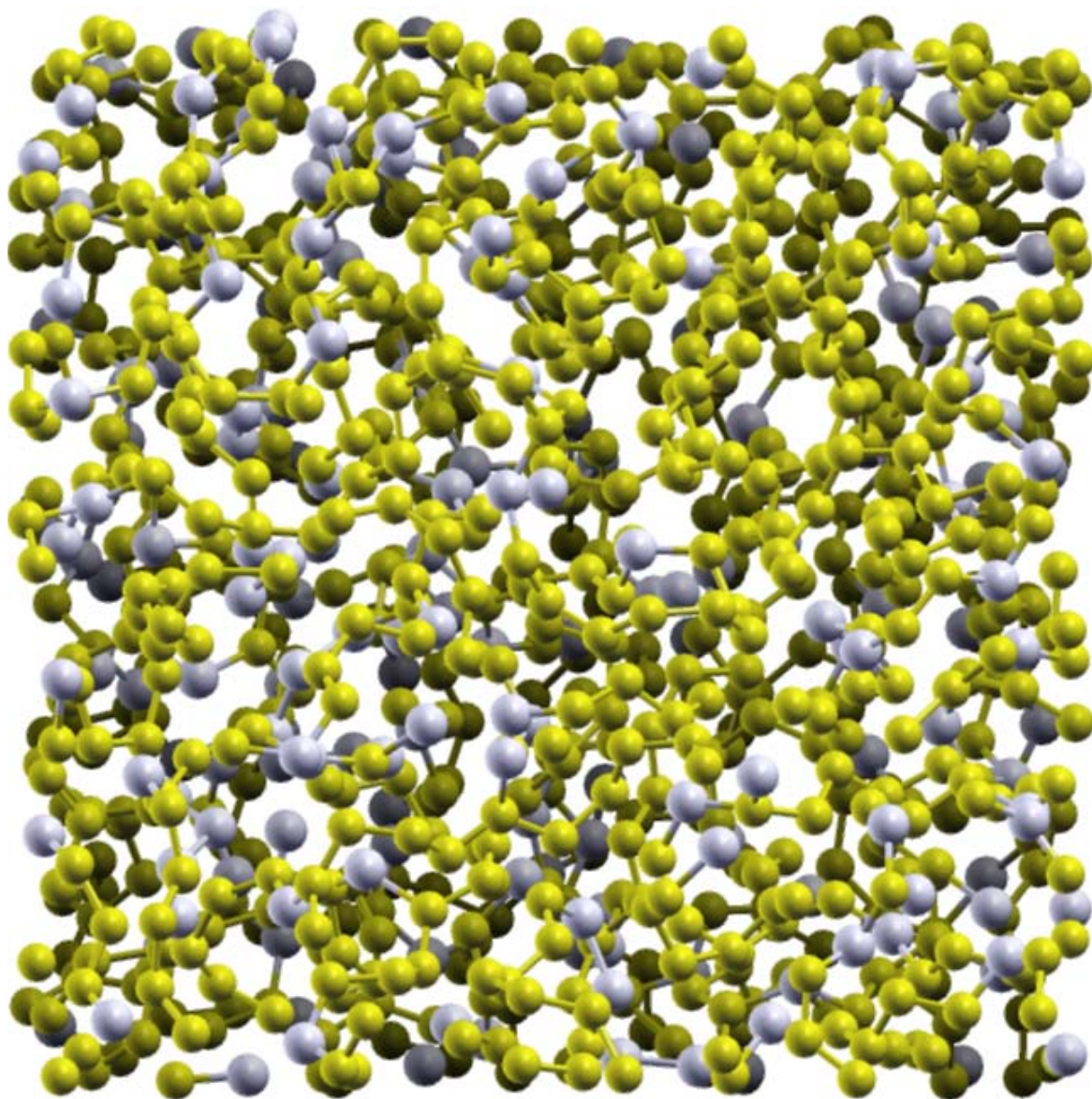


Figure 5.31. Computed structure of $S_{0.8}Se_{0.2}$ glass.

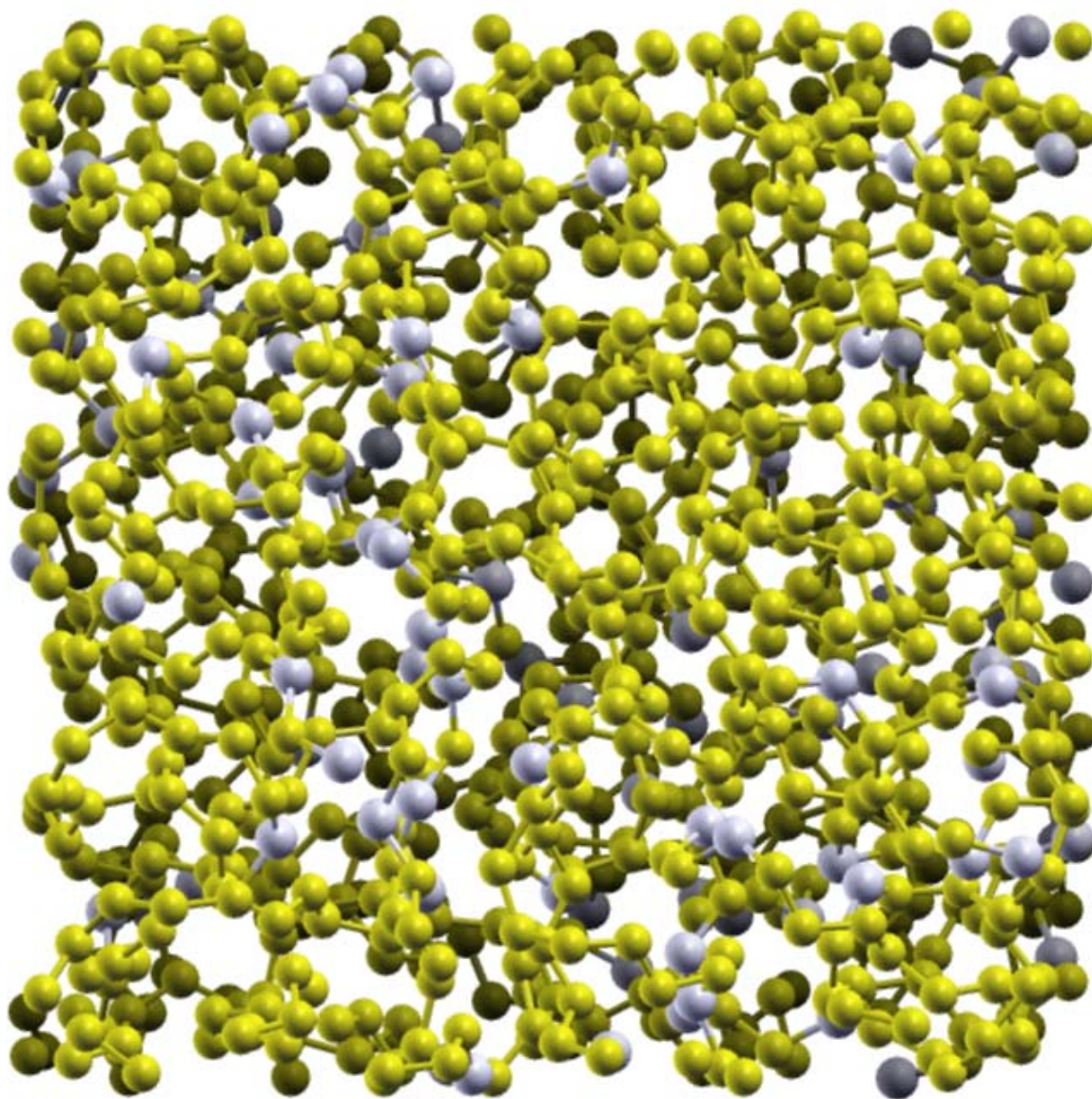


Figure 5.32. Computed structure of $S_{0.9}Se_{0.1}$ glass.

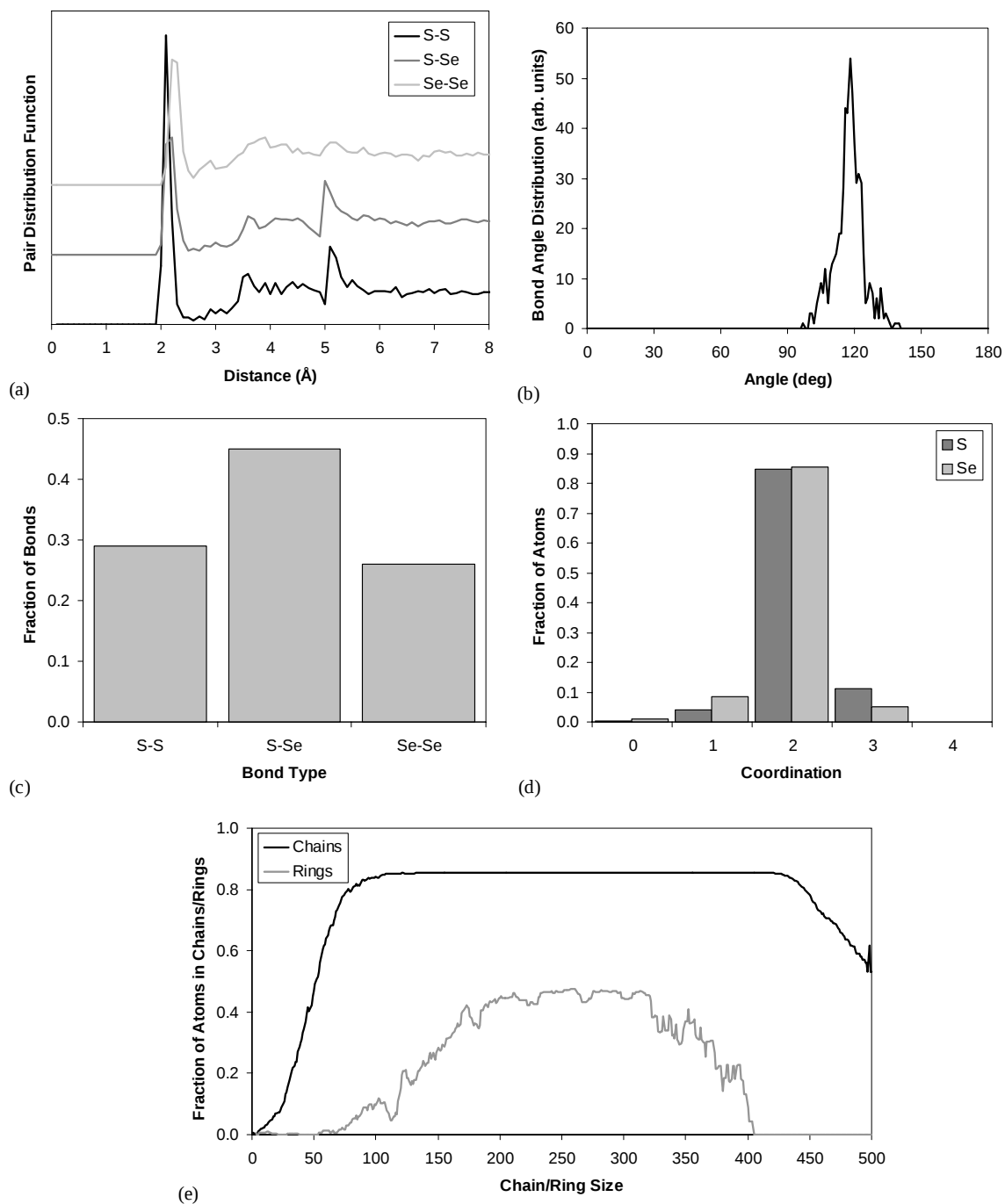


Figure 5.33. Calculated structural data for $S_{0.5}Se_{0.5}$ glass: (a) pair distribution functions, (b) bond angle distribution, (c) bond population, (d) coordination number distribution, and (e) chain/ring length distributions.

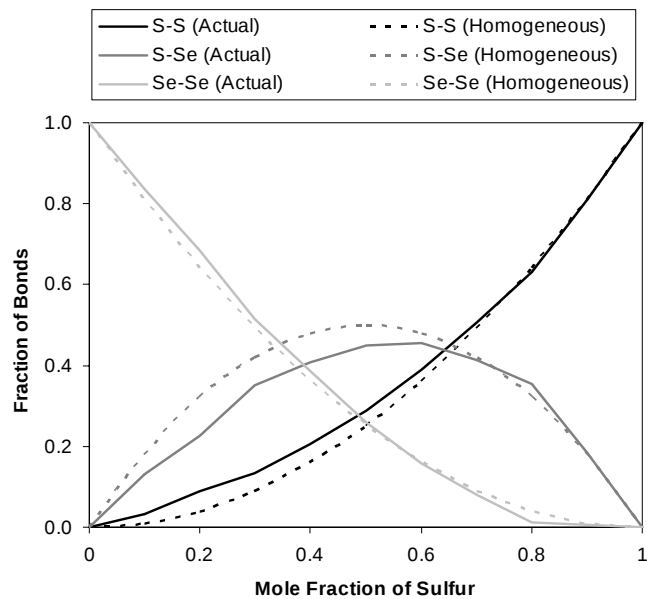


Figure 5.34. Distribution of bond types for glasses in the S_xSe_{1-x} system (solid lines) compared to that of a perfectly homogeneous glass (dashed lines).



Figure 5.35. Average chain length for glasses in the S_xSe_{1-x} system.

5.4 Ge-Se Glasses

The basic structure of the prototypical network glass GeSe_2 , consisting of corner- and edge-sharing $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra, has been well-known since the pioneering neutron diffraction study of Susman *et al.*¹²⁶ and further investigated by subsequent experiments.^{127–129} The resulting model of GeSe_2 glass structure has been supported by numerous molecular dynamics simulations, mostly based on density functional theory (DFT).^{43–48}

However, a recent neutron diffraction experiment by Petri, Salmon, and Fischer¹³⁰ incorporating isotopic substitution has found that $\approx 4\%$ of bonds in GeSe_2 glass are homopolar, breaking with the traditional heteropolar-bonded $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedral motif. Furthermore, in addition to the well-known peak at 2.36 Å in the Ge-Se pair distribution function, Petri and coworkers found a second peak at 3.02 Å. This second peak is attributed to the presence of deformed Ge-centered tetrahedra with three Se atoms at 2.36 Å and a fourth at 3.02 Å. Unfortunately, previous DFT modeling has not been able to capture these details of GeSe_2 structure.

In this section, we use the *ab initio* potentials of Part I in Metropolis Monte Carlo⁶² simulations at the atomistic level to model the structure of Ge-Se glasses, with particular emphasis on GeSe_2 . The Monte Carlo simulations begin by placing 2880 atoms at random positions in a cubic, isochoric simulation space with periodic boundary conditions and a cell length of 44.46 Å. We consider a constant temperature of $T = 298$ K and simulate 40 million trial displacements with a target acceptance rate of 40%.

A plot of the final GeSe_2 glass structure is shown in Figure 5.36, and structural data are plotted in Figure 5.37. The average coordination numbers of the Ge and Se

atoms are 3.97 and 2.04, respectively, very close to the nominal experimental values of 4.0 and 2.0.¹³⁰ While the vast majority of bonds are heteropolar, approximately 3.1% are homopolar Se-Se bonds. This is close to the experimental prediction of $\approx 4\%$ by Petri and coworkers;¹³⁰ however, this value also includes homopolar Ge-Ge bonds, which we did not observe in our simulation. Previous DFT modeling work has found either $>10\%$ homopolar bonding⁴⁴ or none whatsoever.⁴⁸

The predominant structural motif in our simulated GeSe₂ glass is a Ge(Se_{1/2})₄ tetrahedron with an average Ge-Se distance of 2.37 Å and an average Se-Ge-Se bond angle of 104°; the average computed Ge-Se-Ge bond angle is 120°. The tetrahedra are found to be primarily corner-sharing, but a significant number of edge-sharing tetrahedra also exist. The experimentally measured Ge-Se bond distance in this standard tetrahedral configuration is 2.36 Å,¹³⁰ in very close agreement with our simulation results. The computed Se-Ge-Se bond angle of 104° is close to the ideal tetrahedral angle of about 109.5°.

We also find the presence of deformed Ge-centered tetrahedra as proposed by Petri *et al.*,¹³⁰ wherein three Se atoms reside at 2.36 Å from the center Ge with a fourth Se at 3.02 Å. Our modeling predicts deformed Ge-centered tetrahedra with three Se atoms at 2.37 Å and a fourth at 3.04 Å, in very good agreement with the experimental results. Unfortunately, experiments have not hitherto been able to measure the bond angles of these deformed tetrahedra. According to our simulation results, the deformed tetrahedra come in at least three unique configurations with different bond angles, as depicted in Figure 5.38. The presence of 50°, 75°, and 140° bond angles in Figure 5.38 can also be clearly seen in the bond angle distribution of Figure 5.37(b).

The presence of these deformed tetrahedra is also reflected in the Ge-Se pair distribution function in Figure 5.37(a), where a strong peak at 2.37 Å is followed by a weaker peak at 3.04 Å. Previous DFT modeling has not observed this second peak,^{43–48} which is experimentally located at 3.02 Å.¹³⁰ The pair distribution functions for Se-Se and Ge-Ge show small peaks at 2.42 Å and 3.30 Å due to homopolar bonding and edge-sharing tetrahedra, respectively. The Se-Se peak at 2.42 Å is in perfect agreement with experiment, but the Ge-Ge peak at 3.30 Å is at a longer distance than the experimental value of 3.02 Å.¹³⁰

The success of our model at reproducing even the defect structures in GeSe₂ glass can be attributed to its multiscale nature. The use of Møller-Plesset perturbation theory allows for highly accurate energy calculations on small clusters of atoms, allowing for a more accurate description of interatomic interactions than can be provided by DFT. By fitting the discrete set of *ab initio* data to continuous functions, large-scale classical simulations can be run with hundreds or thousands of atoms to provide good statistics for structural analysis. This combination of highly accurate quantum-level calculations with large-ensemble classical simulations can provide a significant advantage over DFT for obtaining accurate structural data.

As shown in Figure 5.39, the fraction of homopolar bonding increases dramatically on either side of GeSe₂ ($\langle m \rangle = 2.67$). This is because GeSe₂ glass achieves the ideal stoichiometry for forming a chemically ordered covalent network (COCN).⁸⁴ As expected, the fraction of Ge-Ge bonds increases for $\langle m \rangle > 2.67$, and the fraction of Se-Se bonds increases for $\langle m \rangle < 2.67$.

5.4.1 Rigidity Percolation

According to the Phillips theory of topological constraints, covalent systems with $\langle m \rangle < 2.4$ exhibit a large number of floppy modes which allow for continuous deformations of the network without any cost in energy.^{70,71} In contrast, covalent systems with $\langle m \rangle > 2.4$ display rigidity percolation where the excess constraints propagate throughout the system making a completely rigid structure with no modes of continuous deformation. The critical value of $\langle m \rangle = m_c = 2.4$ therefore corresponds to a threshold for rigidity percolation.

We can test this theory by computing the Hessian matrix $\mathbf{H}$ for our bulk glasses in the Ge-Se system. The Hessian matrix consists of second derivatives of the total system potential U with respect to the $3N$ atomic coordinates:

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 U}{\partial x_1 \partial x_{3N}} \\ \frac{\partial^2 U}{\partial x_2 \partial x_1} & \frac{\partial^2 U}{\partial x_2^2} & \cdots & \frac{\partial^2 U}{\partial x_2 \partial x_{3N}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial x_{3N} \partial x_1} & \frac{\partial^2 U}{\partial x_{3N} \partial x_2} & \cdots & \frac{\partial^2 U}{\partial x_{3N}^2} \end{pmatrix}_{x_i=x_i^0}. \quad (5.7)$$

We now define b_i and $\mathbf{V}_i$ as the eigenvalues and associated eigenvectors of the Hessian matrix:

$$\mathbf{H}\mathbf{V}_i = b_i\mathbf{V}_i. \quad (5.8)$$

Since $\mathbf{H}$ is a real symmetric matrix, the eigenvalues b_i are real and the eigenvectors $\mathbf{V}_i$ form a complete set. Physically, the values of b_i indicate the curvature of the potential energy landscape in the corresponding $\mathbf{V}_i$ eigendirections. If $b_i \leq 0$, a continuous deformation is possible without any external stimulus. High values of b_i indicate rigid modes where

deformations are only possible with a very high kinetic energy. Low, positive values of b_i indicate soft modes that can be traversed with low kinetic energy, such as that provided by thermal fluctuations at room temperature.

Figure 5.40 plots the number of soft modes ($b_i < 20 \text{ J/m}^2$) normalized to the total number of independent modes available to the system ($3N - 6$). This figure shows evidence in support of a rigidity percolation threshold at $\langle m \rangle = 2.4$: as the average coordination number increases to $\langle m \rangle = 2.4$, the fraction of soft modes decreases dramatically; above $\langle m \rangle = 2.4$, the fraction of soft modes equilibrates quickly, indicating the onset of rigidity percolation.

5.4.2 Glass Surfaces

We prepare Ge-Se glass surfaces by removing periodic boundary conditions in the xy -plane and allowing for surface relaxation via Metropolis Monte Carlo. The initial configuration of atoms is the equilibrated bulk structure. Atoms below $z = 1.5 \text{ nm}$ are frozen in the bulk configuration and not allowed to participate in Monte Carlo displacements. This effectively provides for a bulk glass interface in the lower part of the simulation cell and a free surface at the top.

The surface relaxation process in Ge-Se glasses involves diffusion of selenium atoms to the free surface. This is shown for GeSe_4 in Figure 5.41 and is also true for GeSe_2 , GeSe_3 , GeSe_5 , GeSe_7 , GeSe_{11} , and GeSe_{17} glasses. Since selenium prefers a twofold coordination, it can more easily adopt an exposed configuration at a surface than can a fourfold-coordinated germanium atom. Hence, it is more energetically favorable to form a layer of selenium atoms at a free surface than to have exposed germanium atoms. The Ge remaining in the bulk

glass continues to adopt its tetrahedral coordination. GeSe did not form an obvious Se-rich layer at the surface since selenium is both deficient and highly constrained in this glass.

5.4.3 Nanoindentation and Incipient Plasticity

In order to investigate incipient plasticity as a function of average coordination number, we perform nanoindentation simulations on the Ge-Se glass surfaces from Section 5.4.2. We consider a hard-shell spherical indenter with a radius of 1.0 nm. The indenter starts above the glass surface and is loaded in steps of 0.1 nm to a maximum penetration depth of 1.0 nm. The atoms respond to the indentation with 500,000 Monte Carlo displacements per step of the indenter. After reaching maximum penetration depth, the indenter is unloaded in steps of 0.1 nm back to the original height. Again, 500,000 Monte Carlo displacements are used at each step to allow the glass to relax during removal of the indenter.

Figures 5.42 and 5.43 show cross-sections of the GeSe and GeSe₄ glasses, respectively, during loading of the indenter. Whereas GeSe responds primarily by densification around the indenter, the GeSe₄ glass develops a ring-shaped mound above the original glass surface. Figure 5.44 shows the growth of these mounds during indenter loading and unloading for all of the Ge-Se glasses under consideration. During the initial loading of the indenter, the mound size grows most quickly in glasses with lower average coordination number. These glasses have a greater number of floppy modes, which enable shear flow.

However, floppy modes can also facilitate densification, which plays an increasingly dominant role in low- $\langle m \rangle$ glasses at higher loads. Figure 5.44 shows a crossover point about halfway through the loading process where glasses near the rigidity percolation threshold of

$\langle m \rangle = 2.4$ start to exhibit the greatest mound size. The mound size at maximum indenter penetration is shown in Figure 5.45 as a function of average coordination number. This figure shows a clear maximum at $\langle m \rangle = 2.4$, indicating the greatest shear flow and least densification in the GeSe_4 glass.

According to the Phillips model of topological constraints, systems near the rigidity percolation threshold have an optimized glass structure. This is supported by the critical behavior of incipient plasticity we observe about $\langle m \rangle = 2.4$, where the preferred mode of deformation is shear flow rather than densification. Shear flow allows for displacement, rather than distortion, of the glass structure, thereby preserving its integrity.

The deformation behavior of Ge-Se glasses in the $\langle m \rangle > 2.4$, $\langle m \rangle < 2.4$, and $\langle m \rangle = 2.4$ regimes is further elucidated by Figures 5.46-5.48, which plot cross-sections of the initial glass structures prior to indentation, with arrows indicating atomic displacements after complete loading and unloading of the indenter. The arrows in Figure 5.46 show that GeSe glass ($\langle m \rangle = 3.0$) undergoes densification by short displacements of atoms from the indentation volume. Here there is only a slight movement of atoms upward from the surface. On the other hand, Figure 5.47 shows that atoms in GeSe_{17} glass ($\langle m \rangle = 2.11$) undergo large displacements leading to both densification and mound formation. The ease of atomic motion in this glass is due to the large presence of floppy modes. Finally, Figure 5.48 shows atomic displacements in GeSe_4 glass, which has the optimal value of $\langle m \rangle = 2.4$. GeSe_4 exhibits shear flow through a cooperative upward motion of atoms, with very little densification. This cooperative motion minimizes distortion of the GeSe_4 glass structure as it plastically deforms.

As one final remark, Figure 5.44 shows that the mound sizes remain fairly constant during indenter unloading. The densification induced by the nanoindentation is also found to be irreversible in our simulations. This is in contrast to microindentation experiments on similar systems, where the deformations are predominantly elastic, and plasticity is found to be a minimum at $\langle m \rangle = 2.4$.⁸⁴ This difference between nanoindentation and microindentation behavior is not unexpected since the former operates on an atomistic scale and the latter on a continuum scale. Plastic behavior is known to display a strong size dependence, especially in the sub-micron regime.¹³¹ This is demonstrated by Figures 5.49 and 5.50, which show our simulations of GeSe and GeSe₄ glass during and after indentation with a perfectly flat indenter. As with our previous case of a spherical indenter, we consider a maximum penetration depth of 1.0 nm. Figure 5.49 shows that GeSe glass exhibits only partial elastic recovery after full unloading of the flat indenter. In contrast, Figure 5.50 shows that GeSe₄ glass displays total elastic recovery. A plot of elastic recovery as a function of average coordination number is provided in Figure 5.51. Here we see that elastic recovery is a maximum at $\langle m \rangle = 2.4$, in excellent agreement with microindentation experiments.⁸⁴ This is also consistent with our understanding that GeSe₄ has the ideal glass structure and is hence most resistant to structural deformation. The high- $\langle m \rangle$ glasses exhibit the greatest plasticity due to their excess of topological constraints, which act to frustrate the deformed glass structure.

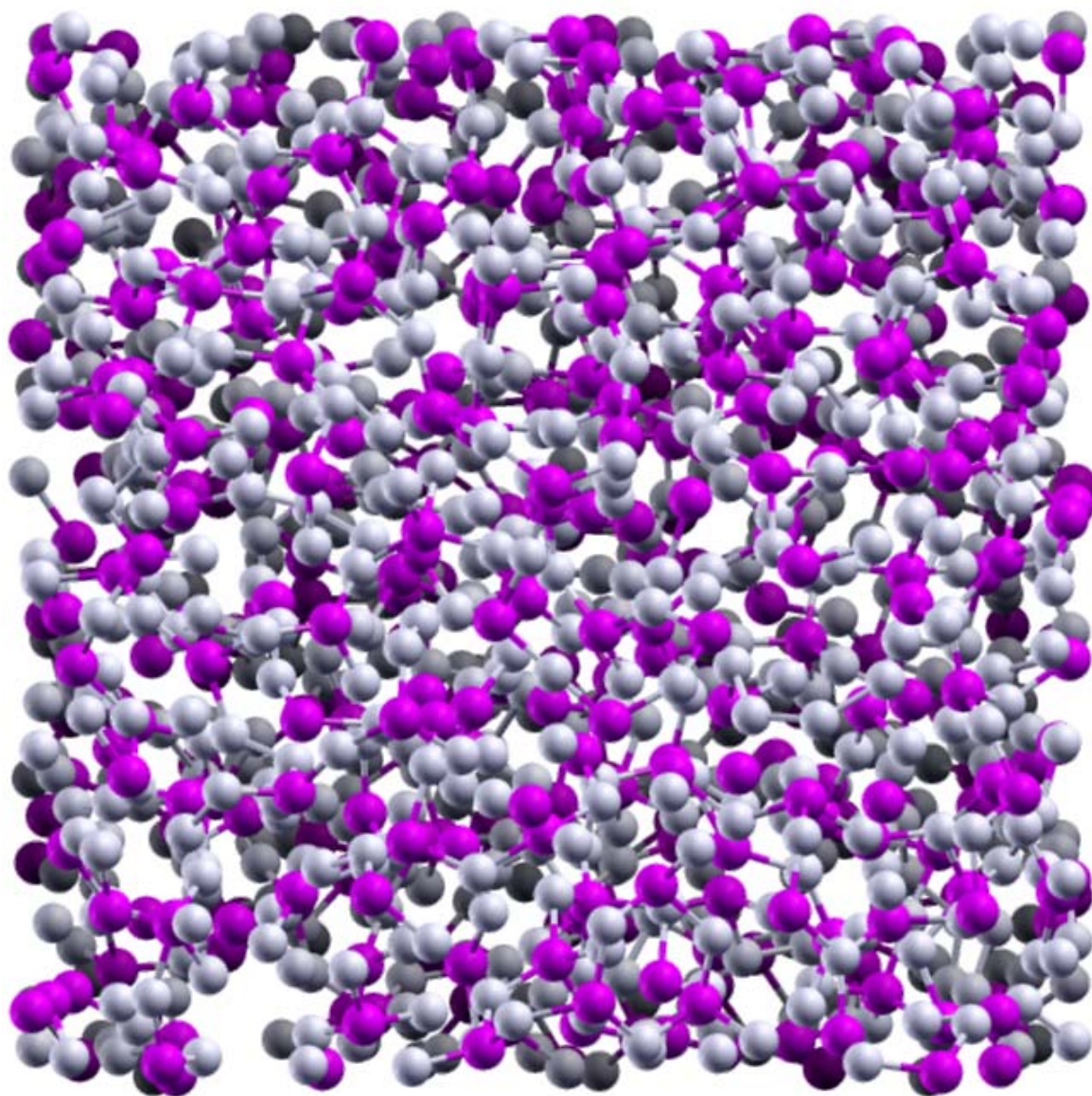


Figure 5.36. Computed structure of GeSe_2 glass.

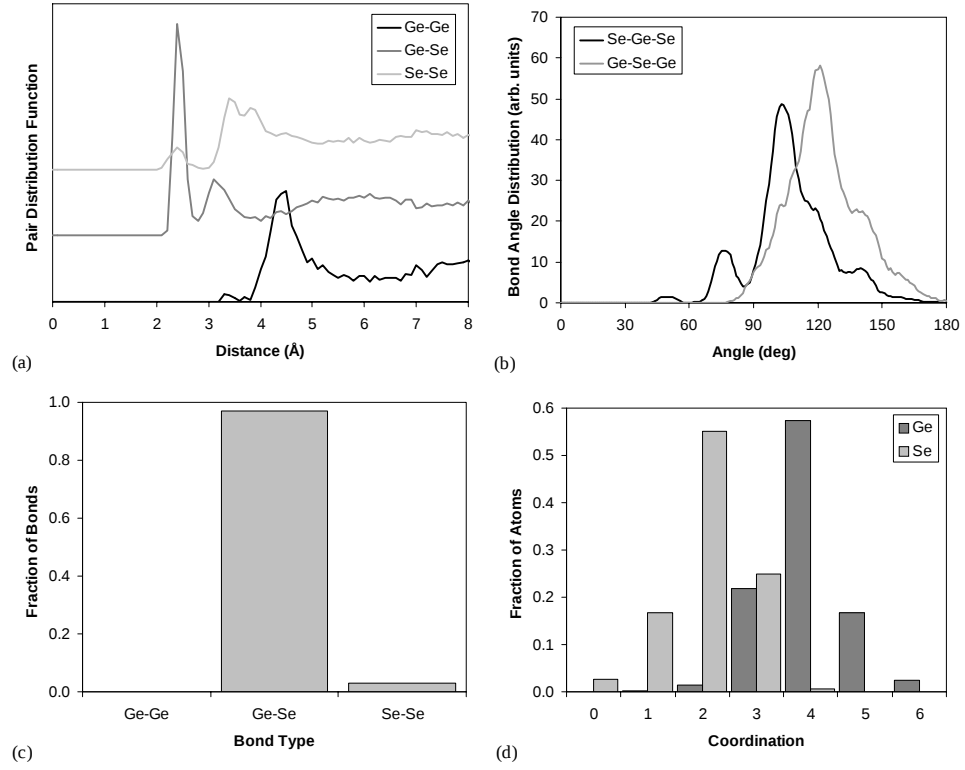


Figure 5.37. Calculated structural data for GeSe_2 glass: (a) pair distribution functions, (b) bond angle distributions, (c) bond population, and (d) coordination number distributions.

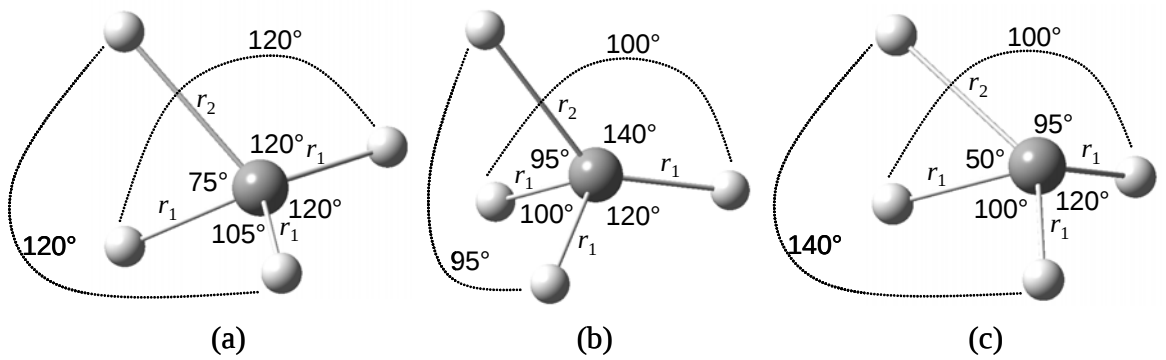


Figure 5.38. Three configurations of deformed $\text{Ge}(\text{Se}_{1/2})_4$ tetrahedra, where $r_1 = 2.37 \text{ \AA}$ and $r_2 = 3.04 \text{ \AA}$.

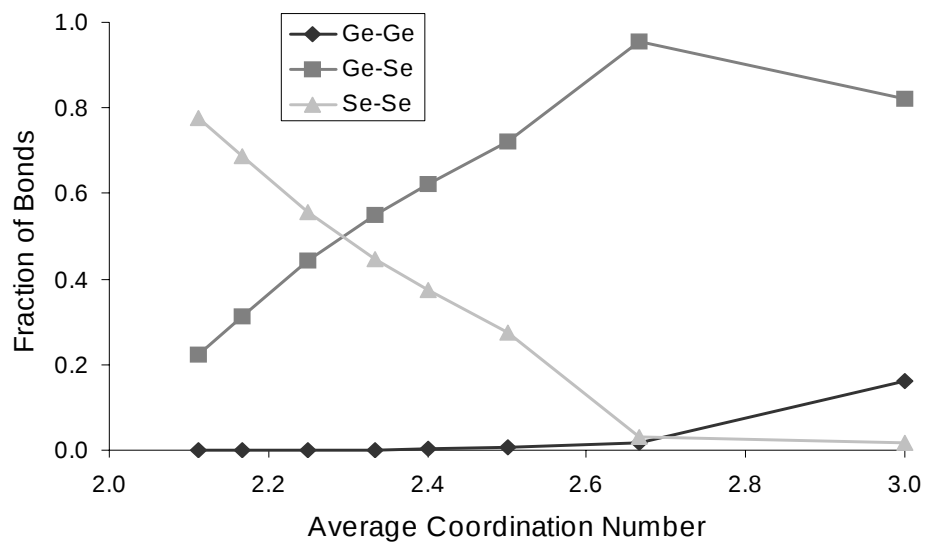


Figure 5.39. Distribution of bond types as a function of average coordination number in Ge-Se glasses.

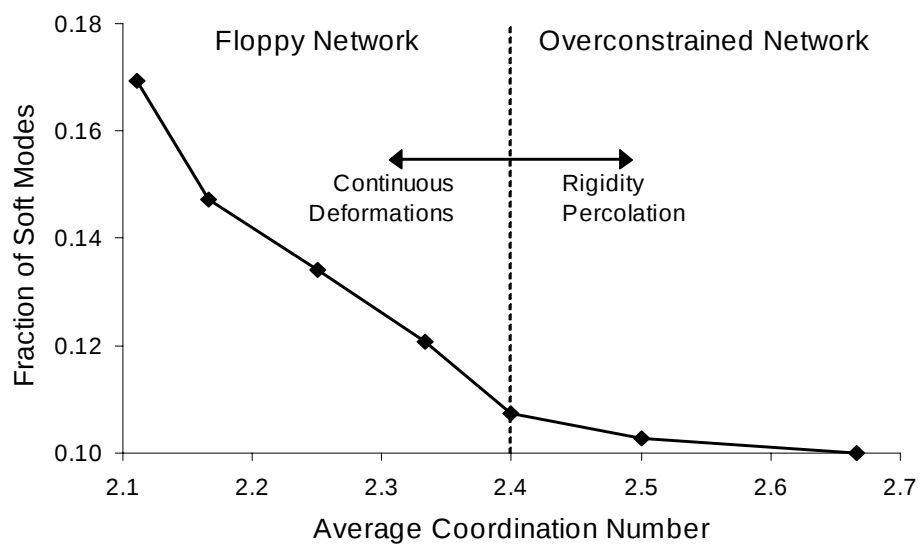


Figure 5.40. Fraction of soft modes as a function of average coordination number for bulk Ge-Se glasses.

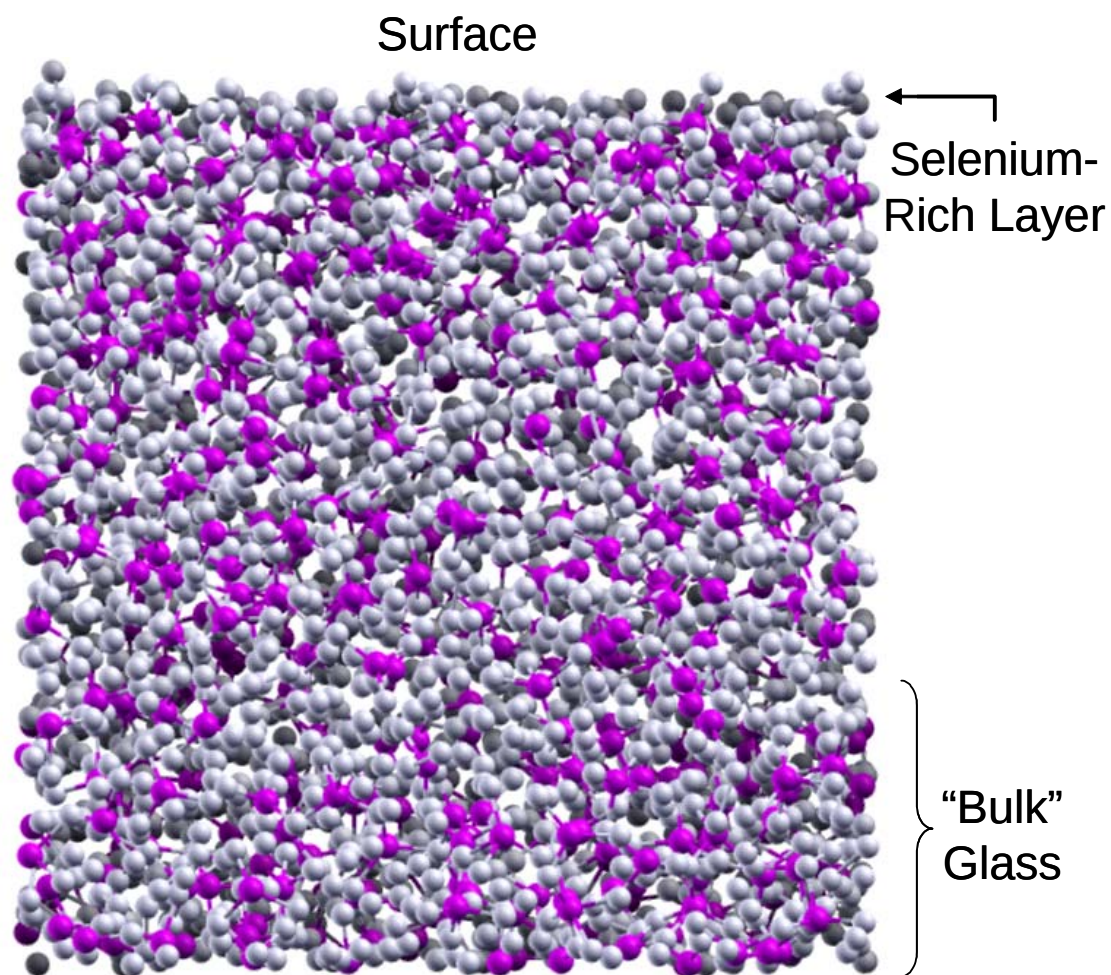


Figure 5.41. Simulated surface of GeSe_4 glass ($44.46 \text{ \AA} \times 44.46 \text{ \AA} \times 44.46 \text{ \AA}$).

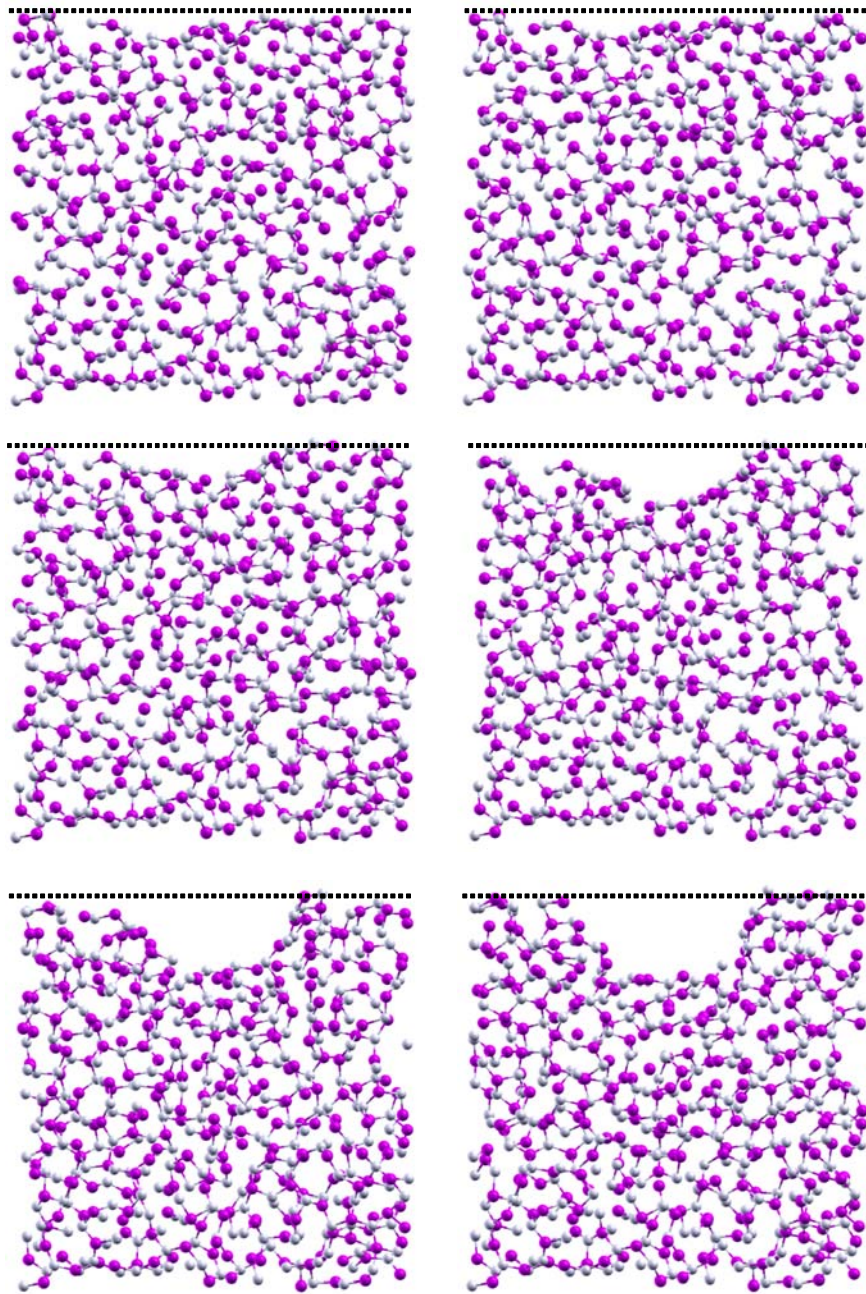


Figure 5.42. Loading of a nanoindenter into the surface of GeSe glass. The dashed lines indicate the initial surface of the glass.

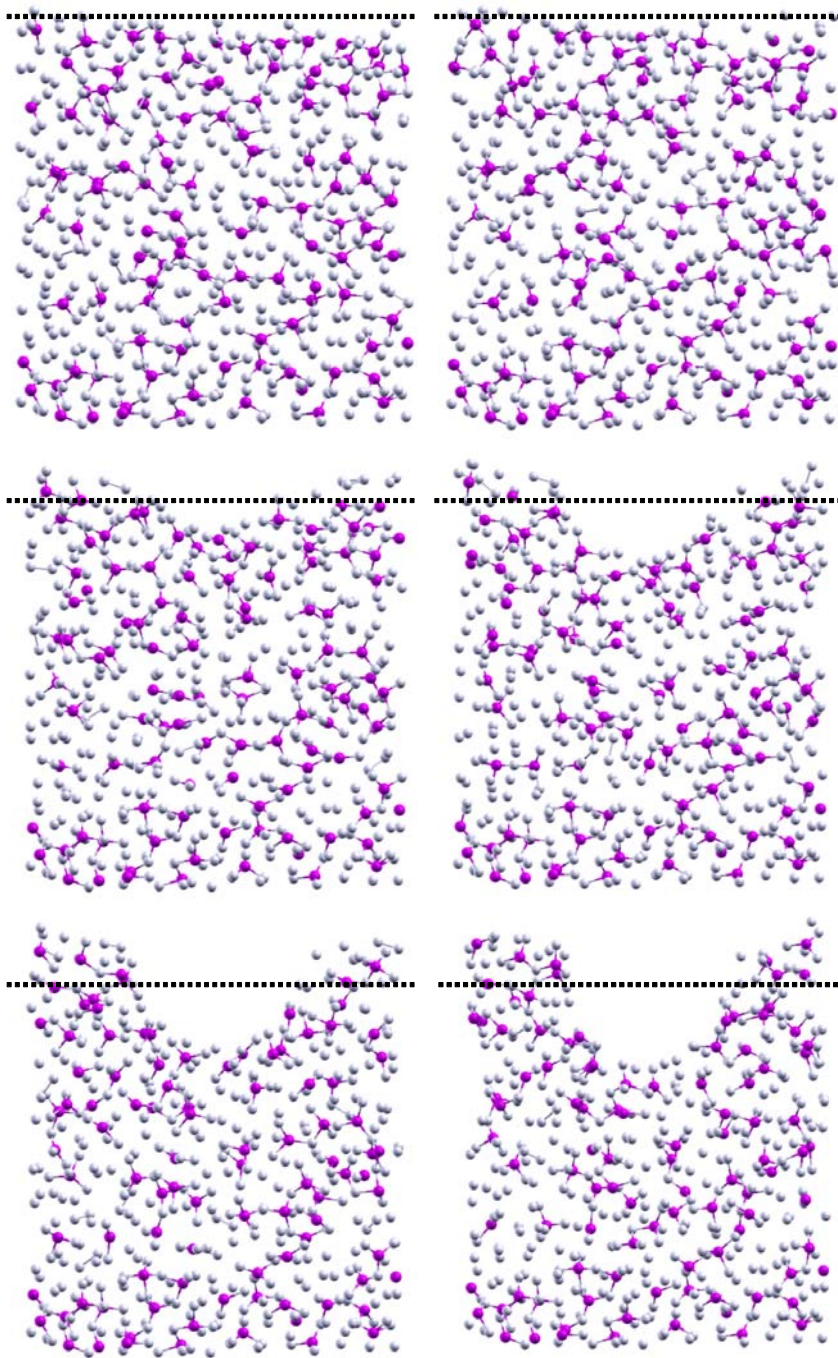


Figure 5.43. Loading of a nanoindenter into the surface of GeSe₄ glass. The dashed lines indicate the initial surface of the glass.

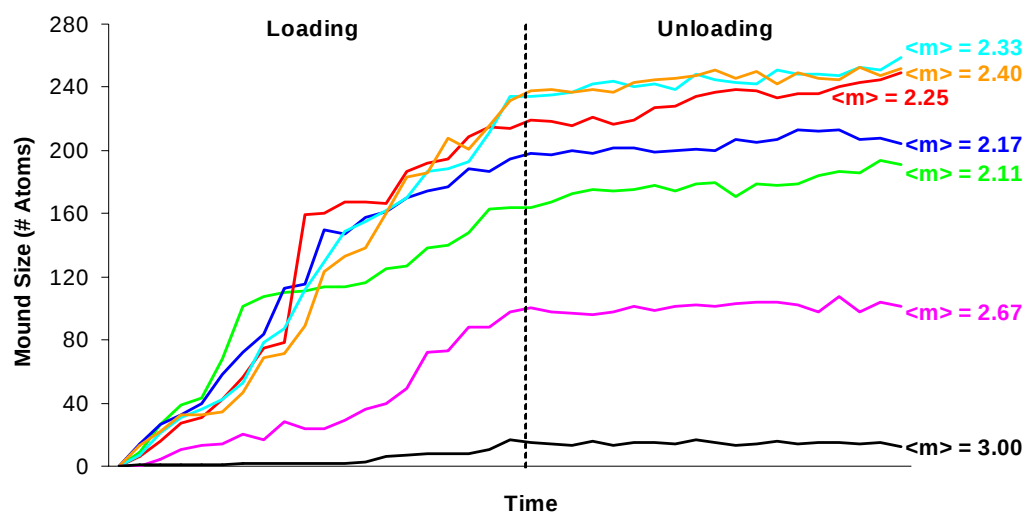


Figure 5.44. Growth of mounds encircling a nanoindentation in Ge-Se glass surfaces with varying average coordination number $\langle m \rangle$.

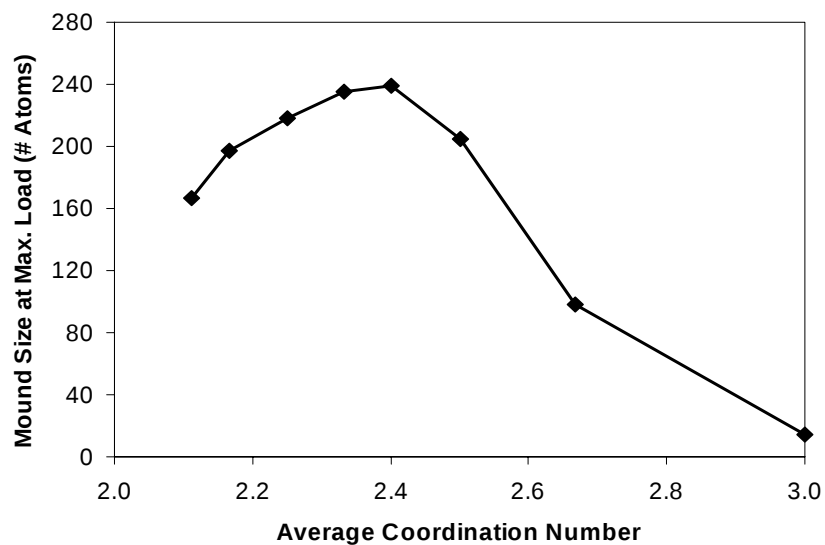


Figure 5.45. Mound size at maximum load as a function of average coordination number for glasses in the binary Ge-Se system.

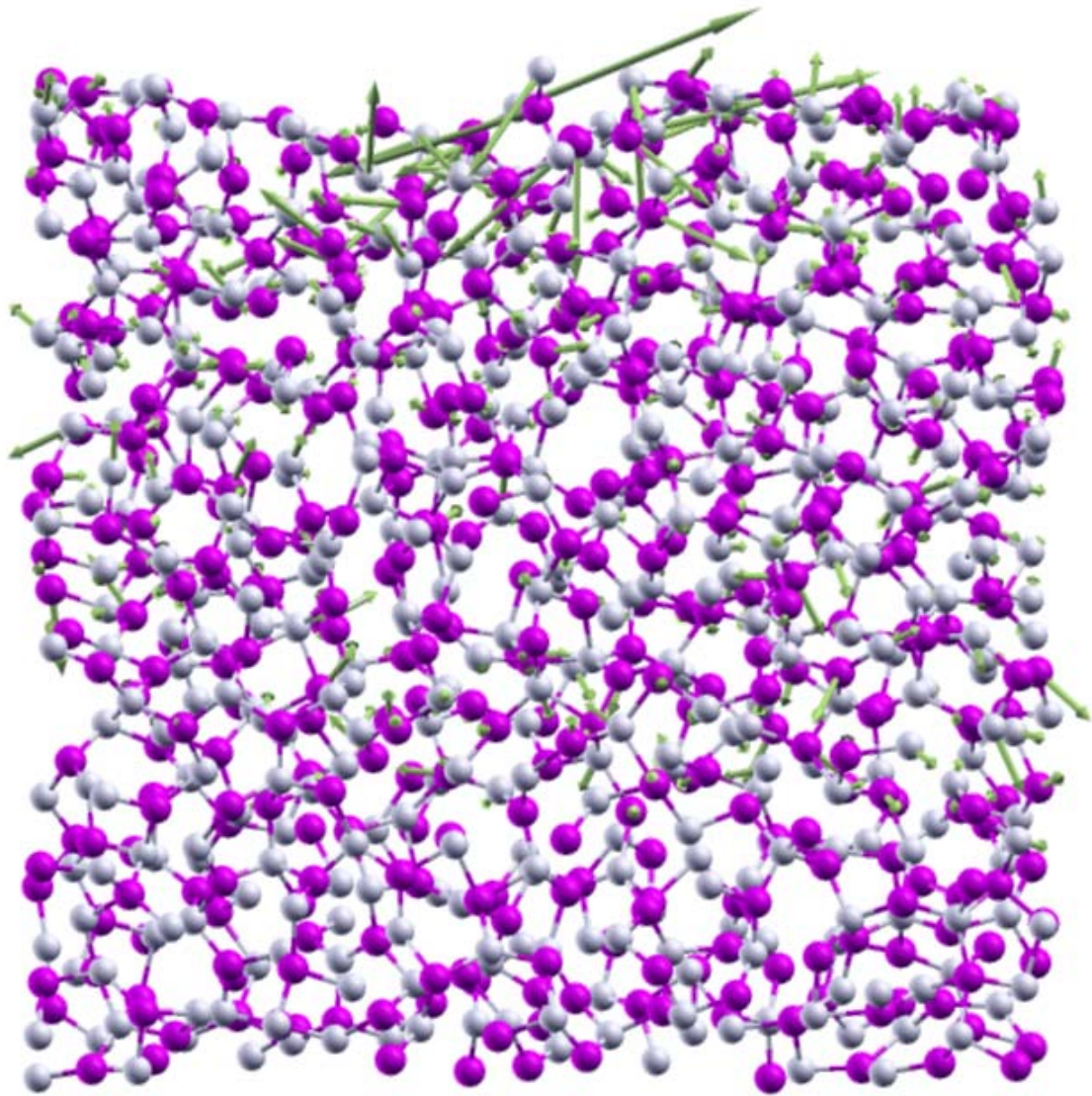


Figure 5.46. Cross-section of GeSe glass ($\langle m \rangle = 3.0$), with vectors indicating atomic displacements after the loading and unloading of a nanoindenter.

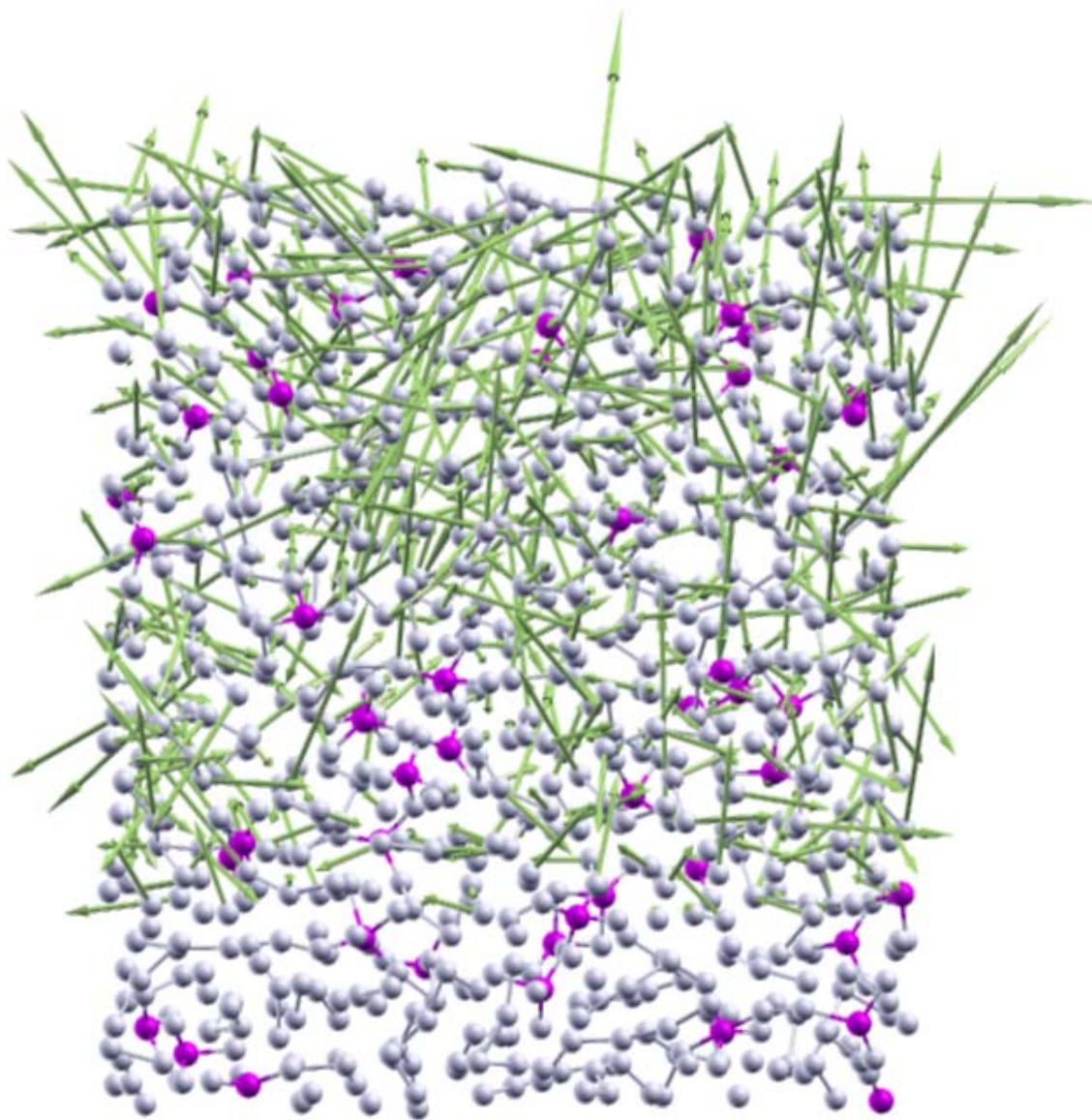


Figure 5.47. Cross-section of GeSe_{17} glass ($\langle m \rangle = 2.11$), with vectors indicating atomic displacements after the loading and unloading of a nanoindenter.

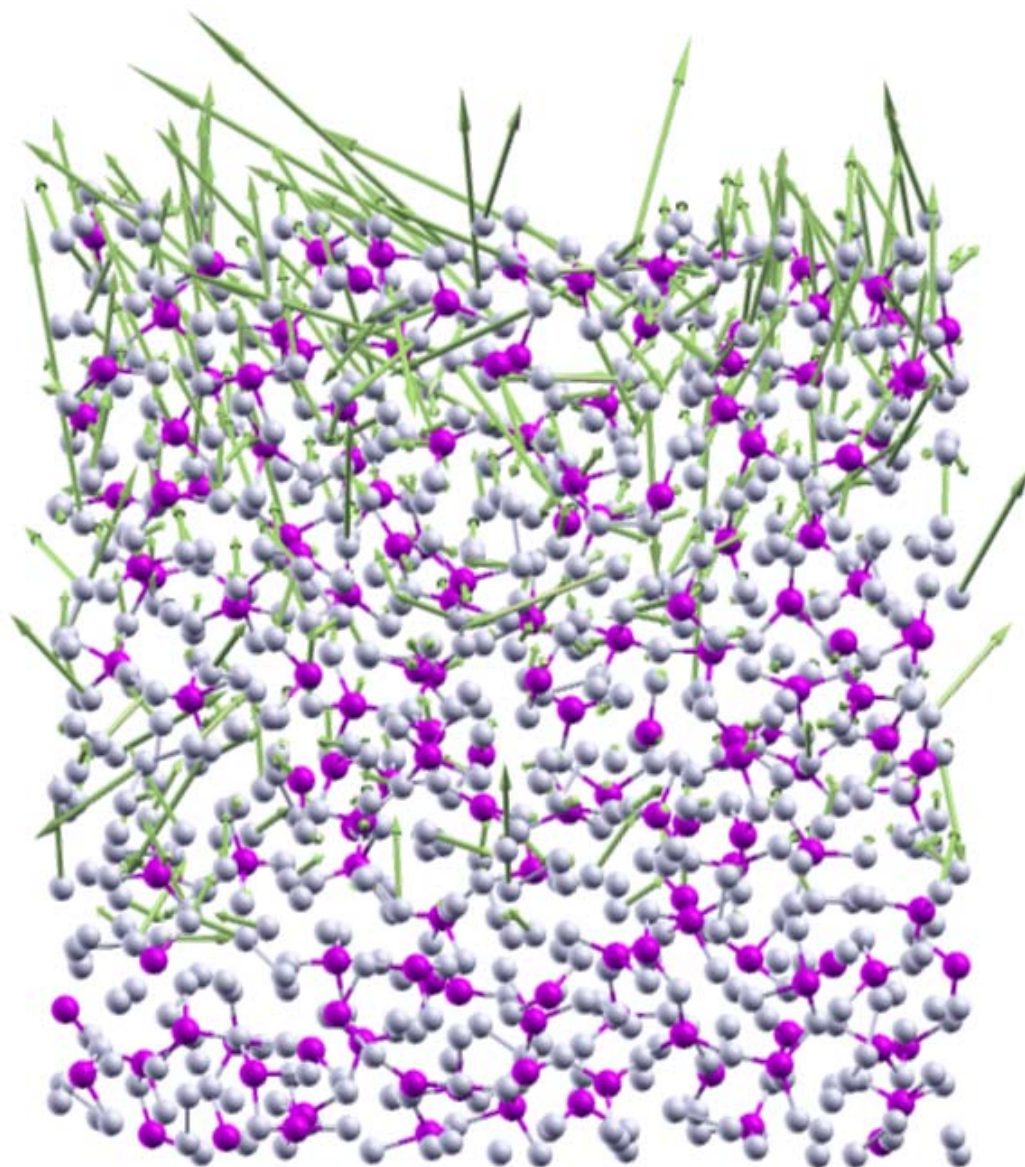


Figure 5.48. Cross-section of GeSe_4 glass ($\langle m \rangle = 2.4$), with vectors indicating atomic displacements after the loading and unloading of a nanoindenter.

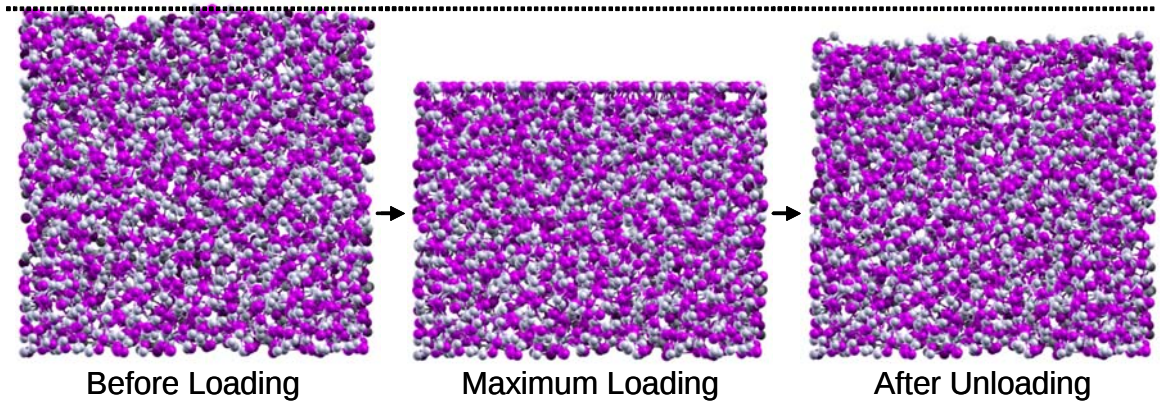


Figure 5.49. Loading and unloading of a flat indenter into the surface of GeSe glass.

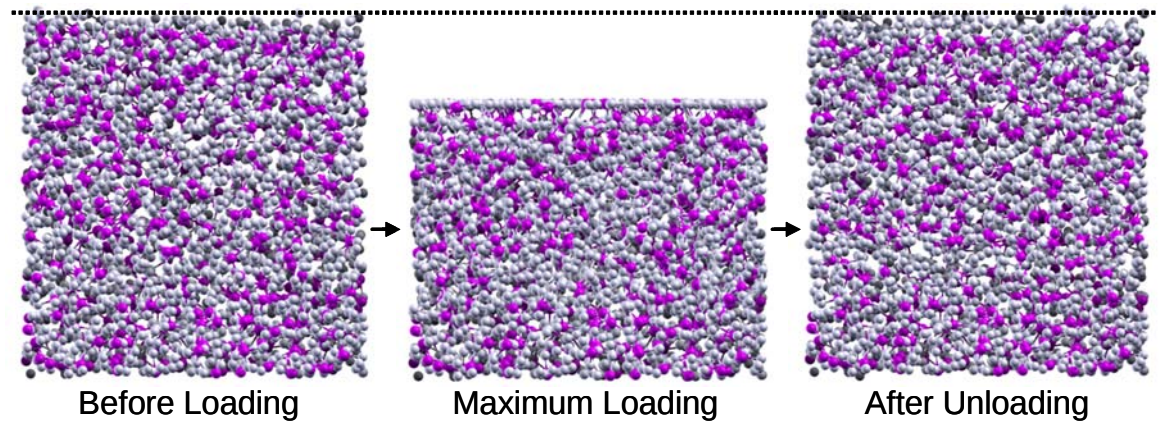


Figure 5.50. Loading and unloading of a flat indenter into the surface of GeSe₄ glass.

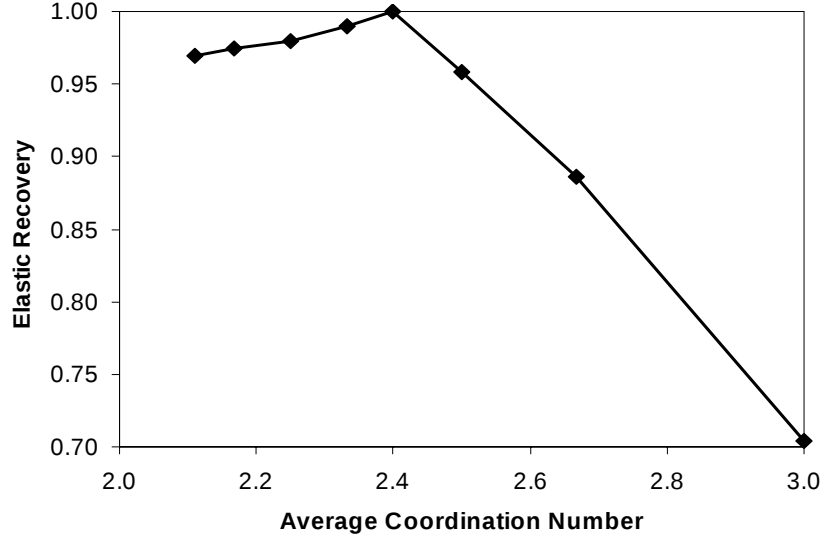


Figure 5.51. Fraction of elastic recovery in Ge-Se glasses after complete loading and unloading of a flat indenter.

5.5 As-Se Glasses

In this section, we model glasses in the As-Se system using Metropolis Monte Carlo simulations together with our *ab initio* potentials. The Monte Carlo simulations begin by placing 1500 atoms at random positions in a cubic, isochoric simulation space with periodic boundary conditions and a cell length of 34.854 Å. We consider a constant temperature of $T = 298$ K and simulate 30 million trial displacements with a target acceptance rate of 40%. The As-Se glass compositions cover a range of average coordination numbers from 2.1 to 2.67.

A plot of the As_2Se_3 glass structure ($\langle m \rangle = 2.4$) is shown in Figure 5.52, and graphs of the structural data are given in Figure 5.53. As expected,^{37,132–139} As_2Se_3 glass consists

of predominantly three-coordinated arsenic and two-coordinated selenium with nearly 100% heteropolar bonding. Experimental measurements indicate an average As-Se bond length of 2.44 Å,¹³³ somewhat shorter than our calculated bond length of 2.55 Å. The experimental Se-Se distance of 3.65 Å¹³³ is slightly longer than our computed value of 3.50 Å. We predict an average As-Se-As bond angle of 104° and an average Se-As-Se bond angle of 116°.

The chemical order of As-Se glasses is remarkably perseverant with respect to compositional variations about $\langle m \rangle = 2.4$. Figure 5.54 shows the computed structure of AsSe₂ glass ($\langle m \rangle = 2.33$), and Figure 5.55 shows the computed structural data. As with As₂Se₃, nearly 100% of the bonds are heteropolar. A recent experiment by Georgiev, Boolchand, and Micoulaut¹⁴⁰ suggested that Se-rich compositions in the As-Se glassy system exhibit tetrahedrally-coordinated arsenic atoms where a fourth selenium atom has a “double” bond to the center arsenic. This suggestion is in agreement with our computed structure of AsSe₂, where we observe both an increased number of four-coordinated arsenic and one-coordinated selenium atoms compared to As₂Se₃.

This propensity for heteropolar bonding is also demonstrated by the arsenic-rich AsSe glass ($\langle m \rangle = 2.5$), shown in Figures 5.56 and 5.57. Here, selenium adopts a three-coordinated arsenic-like character in order to preserve heteropolar bonding. This system has not yet been the subject of a thorough experimental study, but if our modeling results are any indication, AsSe should provide for a very interesting study.

Figure 5.58 plots the fraction of soft modes in As-Se glasses as a function of average coordination number. The As-Se system exhibits a somewhat shallower rigidity transformation compared to Ge-Se glasses (Figure 5.40). While we have drawn the rigidity

percolation threshold at $\langle m \rangle = 2.4$ in Figure 5.58, it could arguably be placed closer to $\langle m \rangle = 2.3$. Such an early onset of rigidity percolation is consistent with the experimental measurements of Georgiev, Boolchand, and Micoulaut,¹⁴⁰ who found an onset of rigidity percolation at $\langle m \rangle = 2.29$.

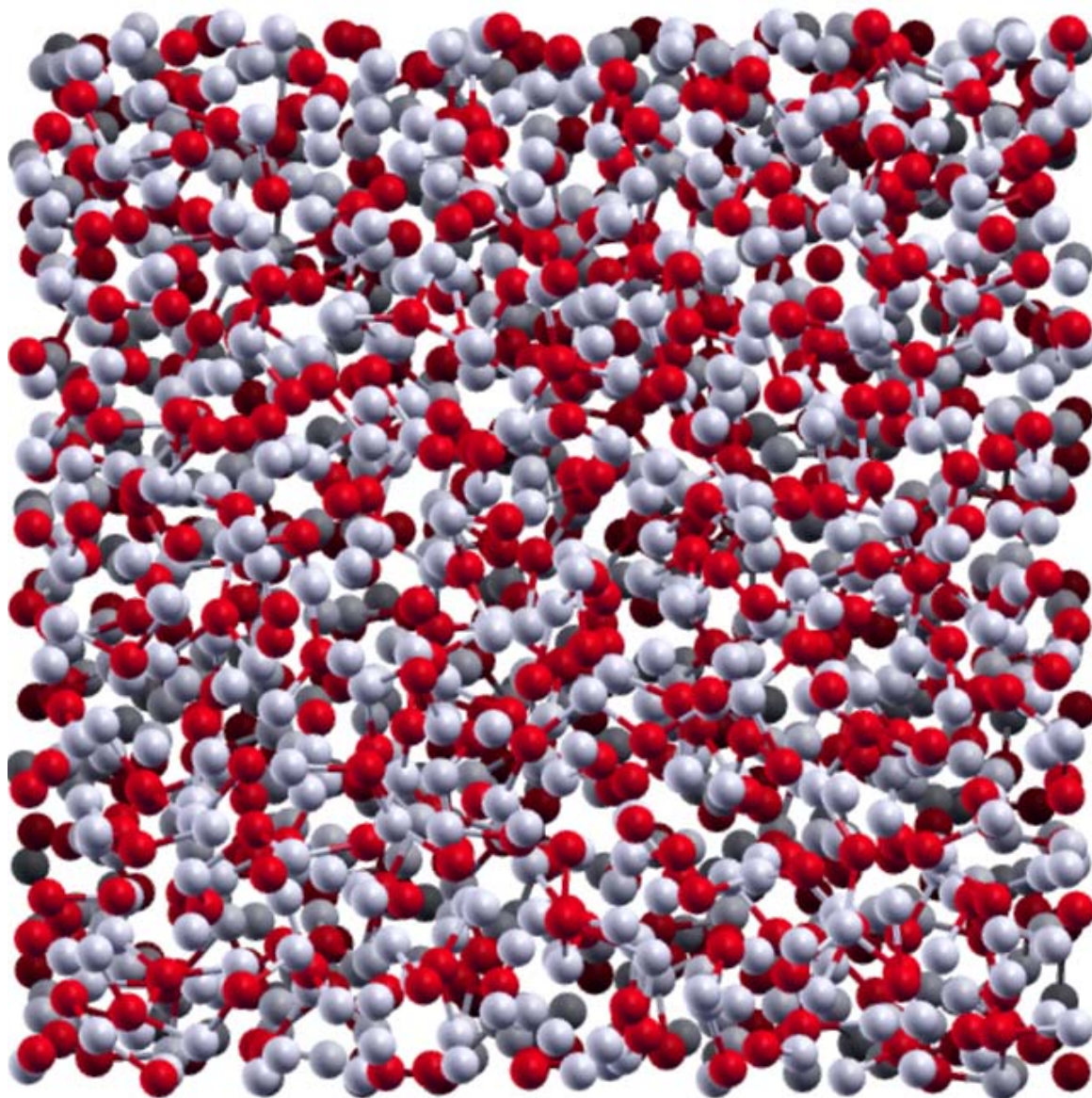


Figure 5.52. Computed structure of As_2Se_3 glass.

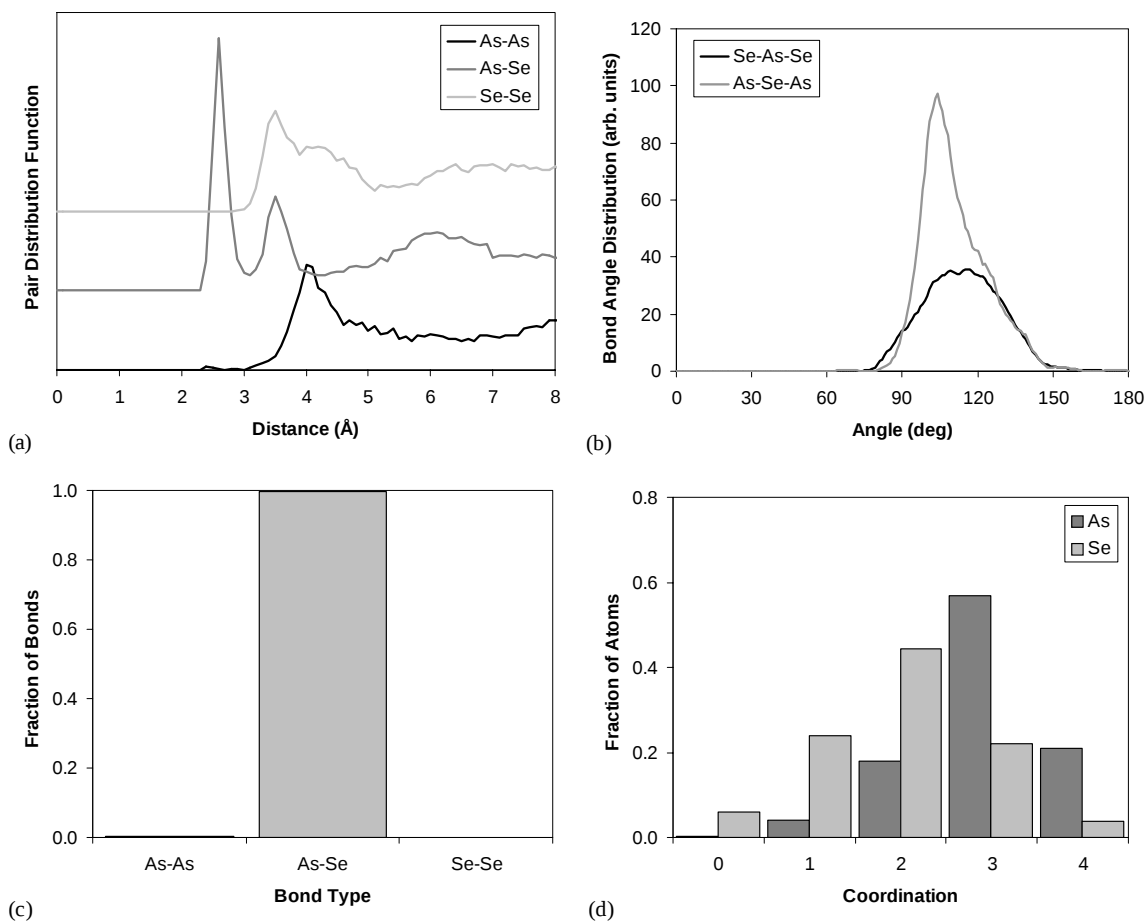


Figure 5.53. Calculated structural data for As_2Se_3 glass: (a) pair distribution functions, (b) bond angle distributions, (c) bond population, and (d) coordination number distributions.

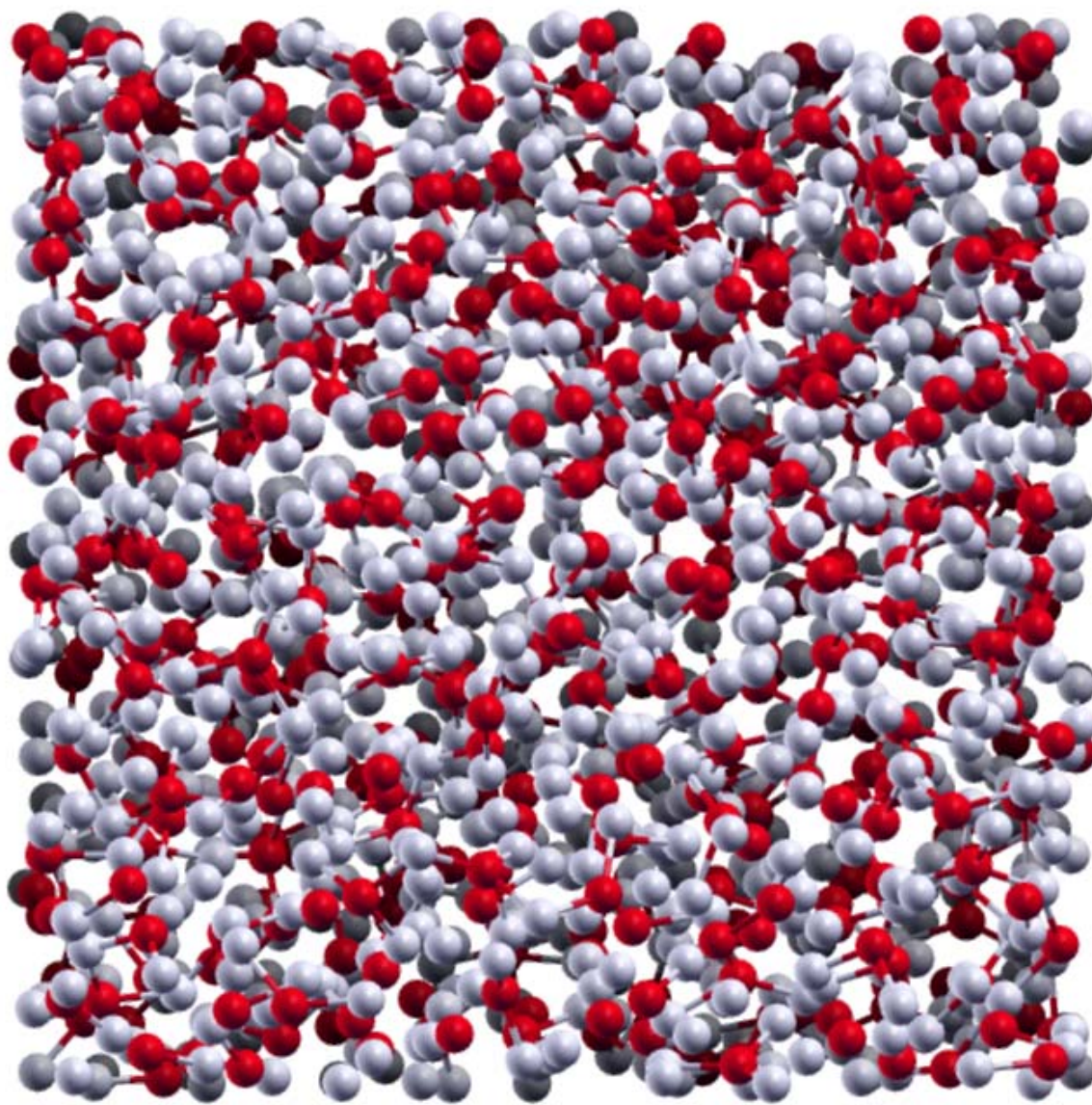


Figure 5.54. Computed structure of AsSe_2 glass.

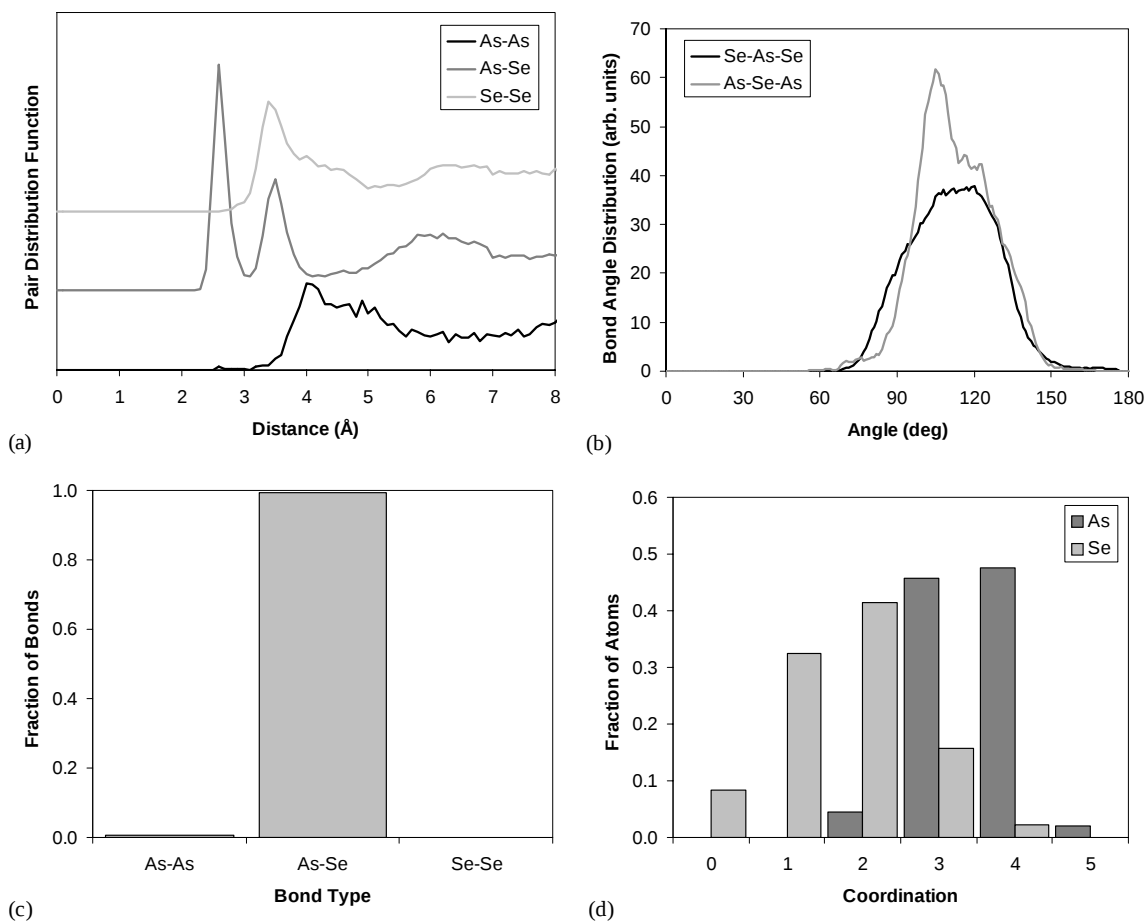


Figure 5.55. Calculated structural data for AsSe₂ glass: (a) pair distribution functions, (b) bond angle distributions, (c) bond population, and (d) coordination number distributions.

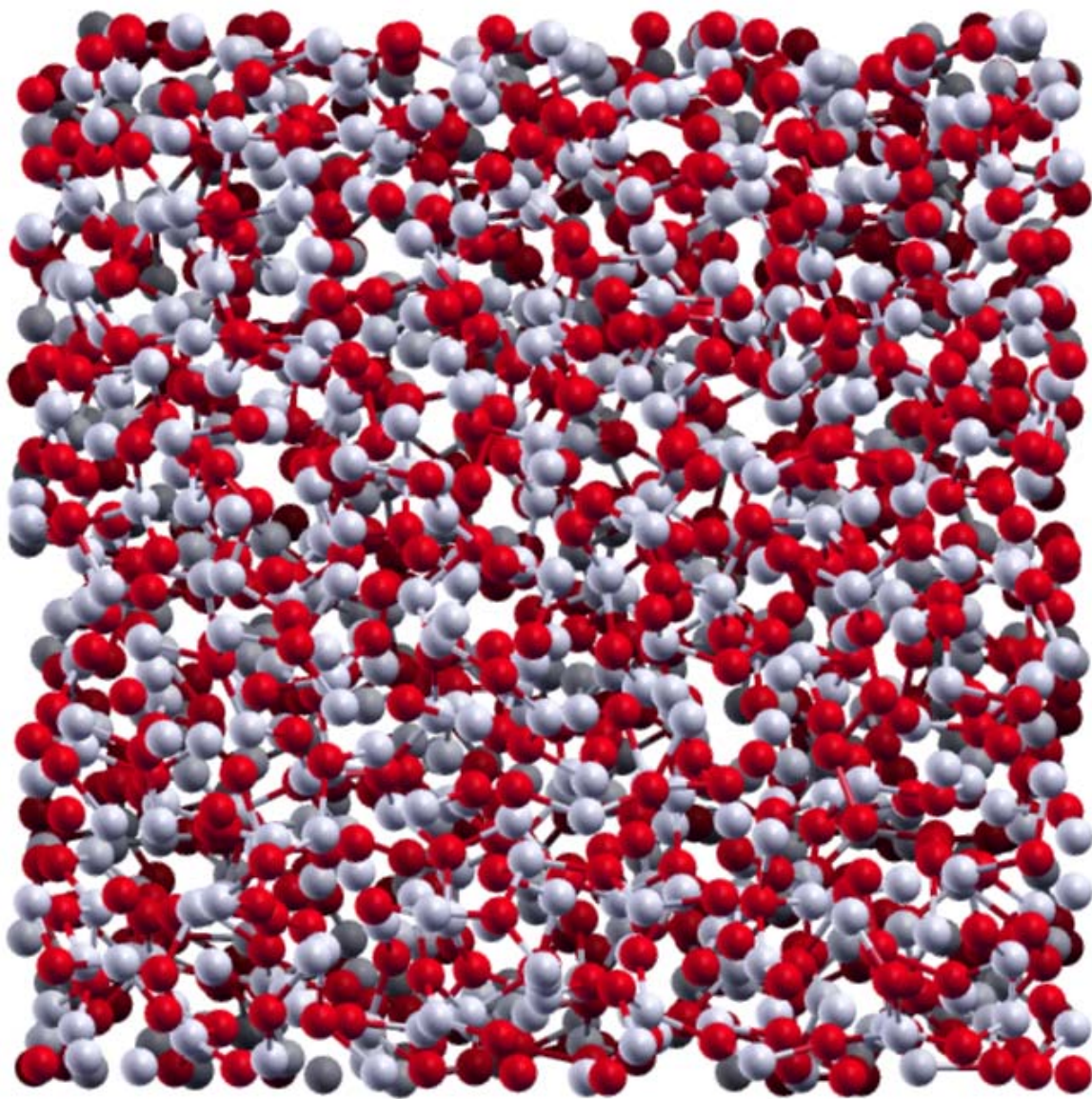


Figure 5.56. Computed structure of AsSe glass.

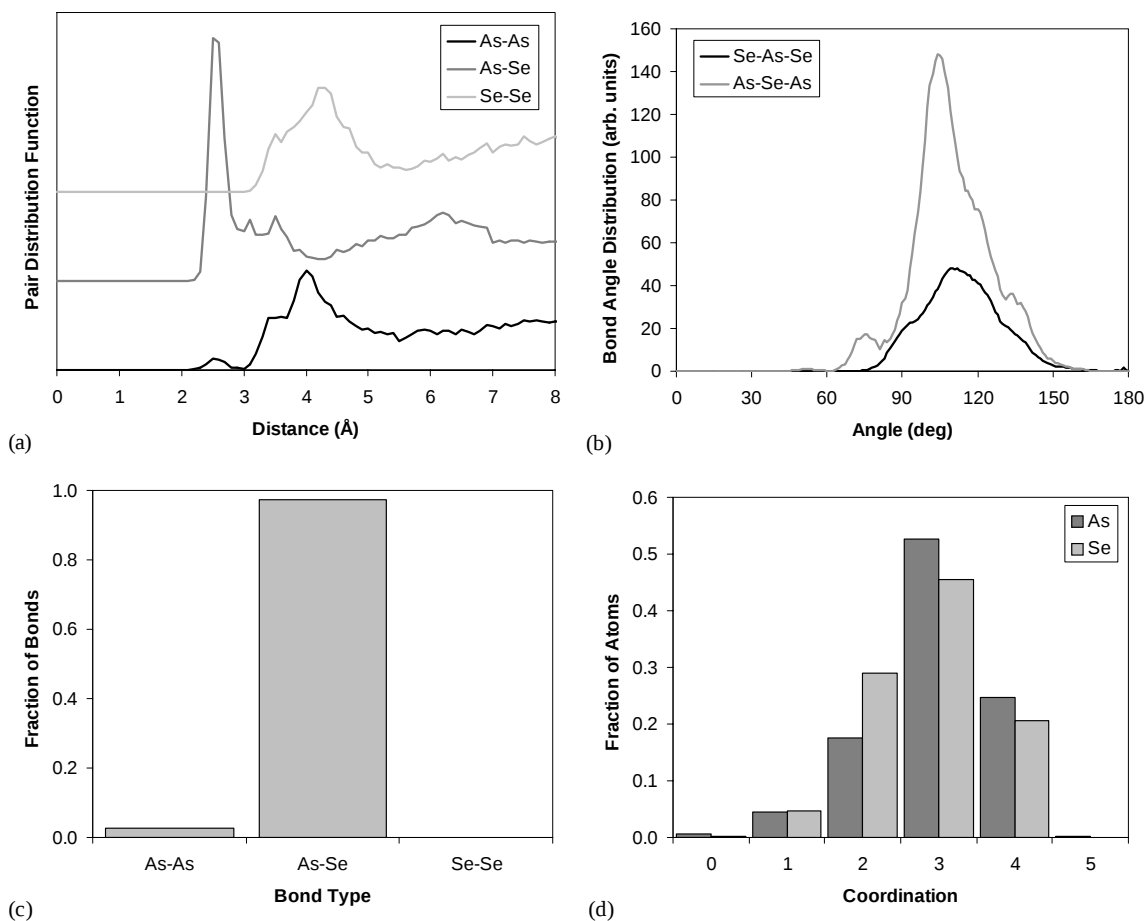


Figure 5.57. Calculated structural data for AsSe glass: (a) pair distribution functions, (b) bond angle distributions, (c) bond population, and (d) coordination number distributions.

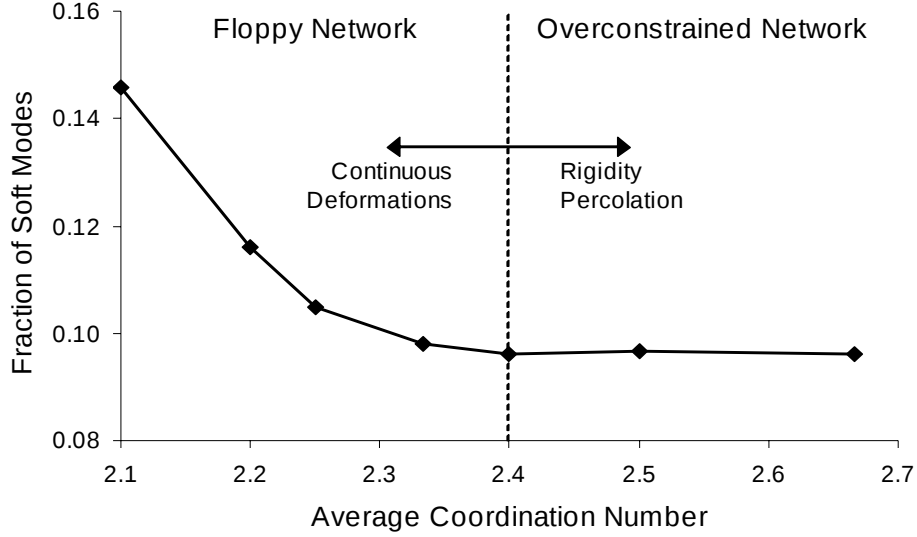


Figure 5.58. Fraction of soft modes as a function of average coordination number for bulk As-Se glasses.

5.6 Ge-As-Se Glasses

Finally, we simulate the structure of several glasses in the Ge-As-Se ternary using Metropolis Monte Carlo and our *ab initio* potentials: GeAsSe₁₃ ($\langle m \rangle = 2.2$), GeAsSe₈ ($\langle m \rangle = 2.3$), GeAs₂Se₇ ($\langle m \rangle = 2.4$), Ge₂AsSe₇ ($\langle m \rangle = 2.5$), Ge₂As₂Se₆ ($\langle m \rangle = 2.6$), and Ge₄As₄Se₇ ($\langle m \rangle = 2.8$), covering a range of average coordination numbers from 2.2 to 2.8. The Monte Carlo simulations begin by placing 1500 atoms at random positions in a cubic, isochoric simulation space with periodic boundary conditions and a cell length of 35.7748 Å. We consider a constant temperature of $T = 298$ K and simulate 30 million trial displacements with a target acceptance rate of 40%.

The resulting glass structures are plotted in Figures 5.59 through 5.64. These

plots show evidence for regions of pure selenium interspersed with regions of higher As and Ge content, particularly in the low- $\langle m \rangle$ glasses (with high Se content). Figure 5.65 plots the fraction of homopolar and heteropolar bonds in the Ge-As-Se system as a function of average coordination number. Here we see that homopolar bonding is predominant with $\langle m \rangle < 2.4$ and heteropolar bonding dominates with $\langle m \rangle > 2.5$. This is consistent with the presence of high-Se regions in the low- $\langle m \rangle$ glasses.

Figure 5.66 plots the fraction of soft modes in the Ge-As-Se system as a function of average coordination number. Unlike for the binary Ge-Se and As-Se glasses, we do not observe a rigidity transformation in the ternary Ge-As-Se system in the region of $2.2 \leq \langle m \rangle \leq 2.8$. This can be explained by Figure 5.67, which shows the computed average coordinations of Ge, As, and Se atoms for the compositions under study. Here we observe a steady increase in the atomic coordinations as the ideal average coordination number of the glass increases. This leads to a higher actual value of $\langle m \rangle$ for these glasses compared to what is predicted using the nominal coordinations of $m_{\text{Ge}} = 4$, $m_{\text{As}} = 3$, and $m_{\text{Se}} = 2$.

Figure 5.68 plots our computed $\langle m \rangle$ versus their corresponding ideal values. Whereas GeAsSe₁₃ glass has an ideal average coordination number of $\langle m \rangle_{\text{ideal}} = 2.2$, we compute an actual average coordination number of $\langle m \rangle_{\text{actual}} = 2.4$. Hence, the Ge-As-Se ternary system exhibits a nonlinear (quadratic) behavior of actual coordination number with composition, effectively lowering the rigidity percolation threshold to a composition having $\langle m \rangle_{\text{ideal}} = 2.2$.

Experimentally, the issue of rigidity percolation in the Ge-As-Se system is still a matter of debate.^{76,90,94,141–144} Regardless of the ultimate outcome in this matter, our

simulations show the importance of considering the actual average coordination number of a glass instead of just its ideal value. This is also important for chalcogenide systems that exhibit molecular clustering, where free molecules in a glass can have an effective coordination of zero.

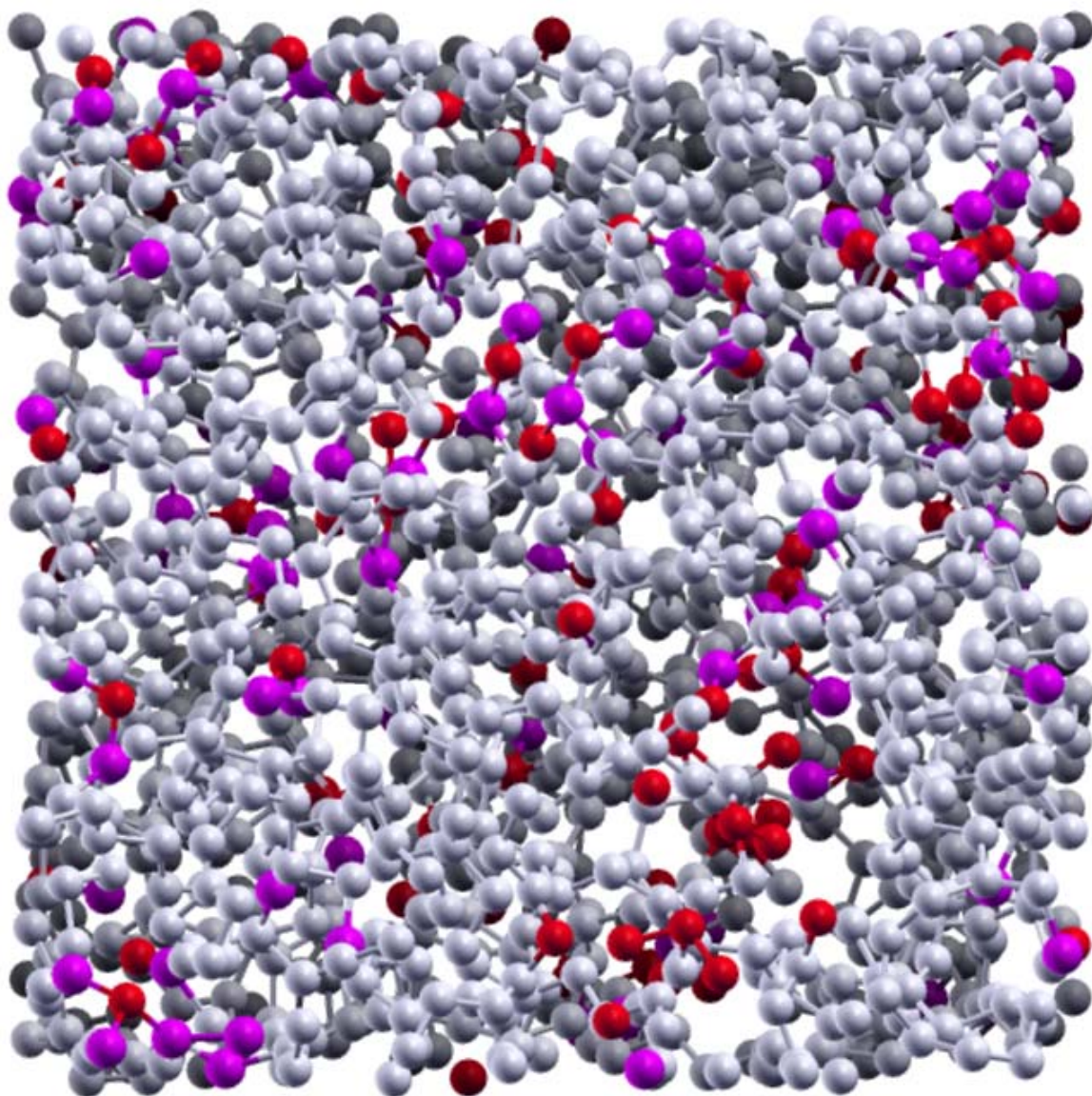


Figure 5.59. Computed structure of GeAsSe_{13} glass.

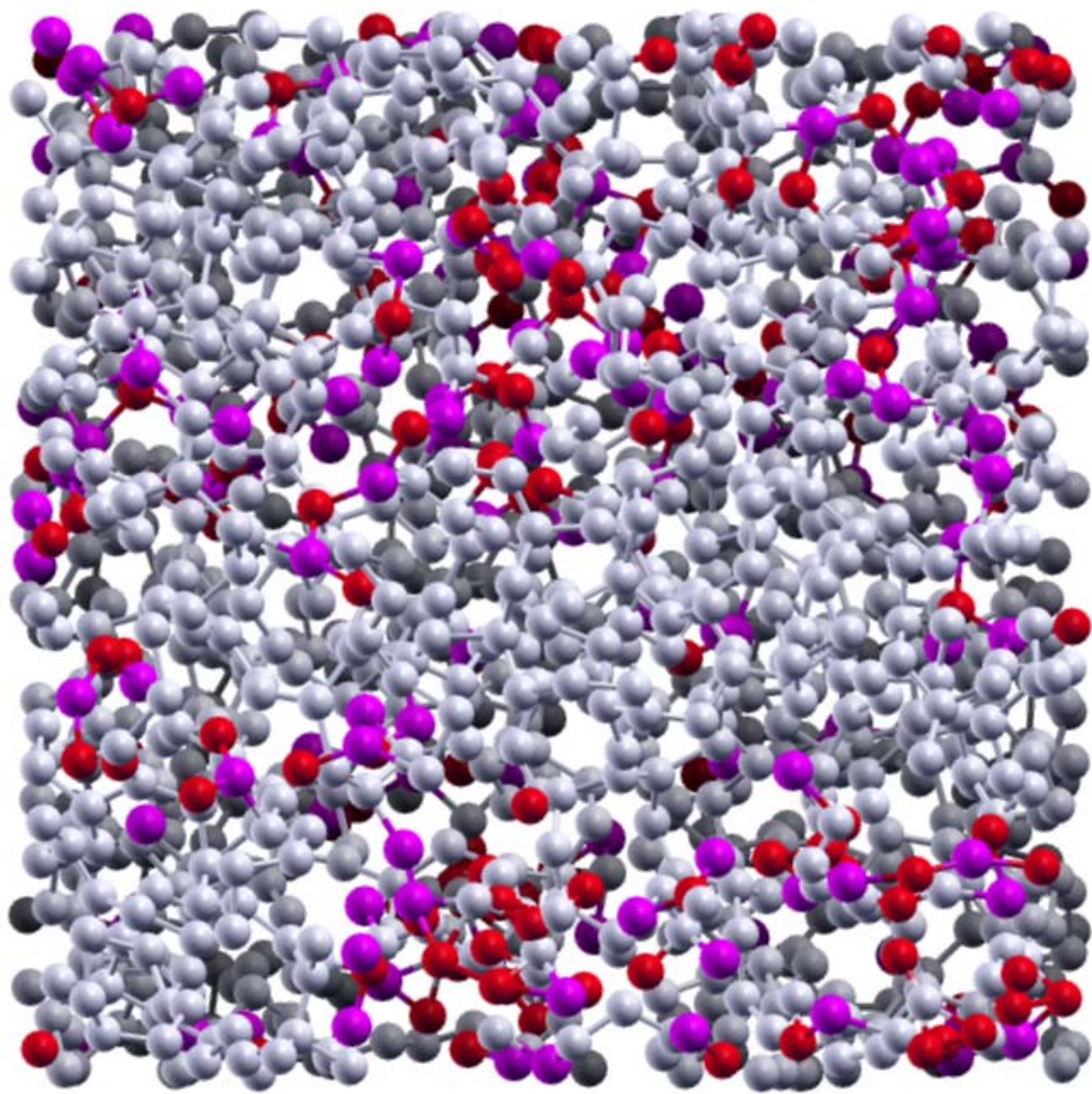


Figure 5.60. Computed structure of GeAsSe₈ glass.

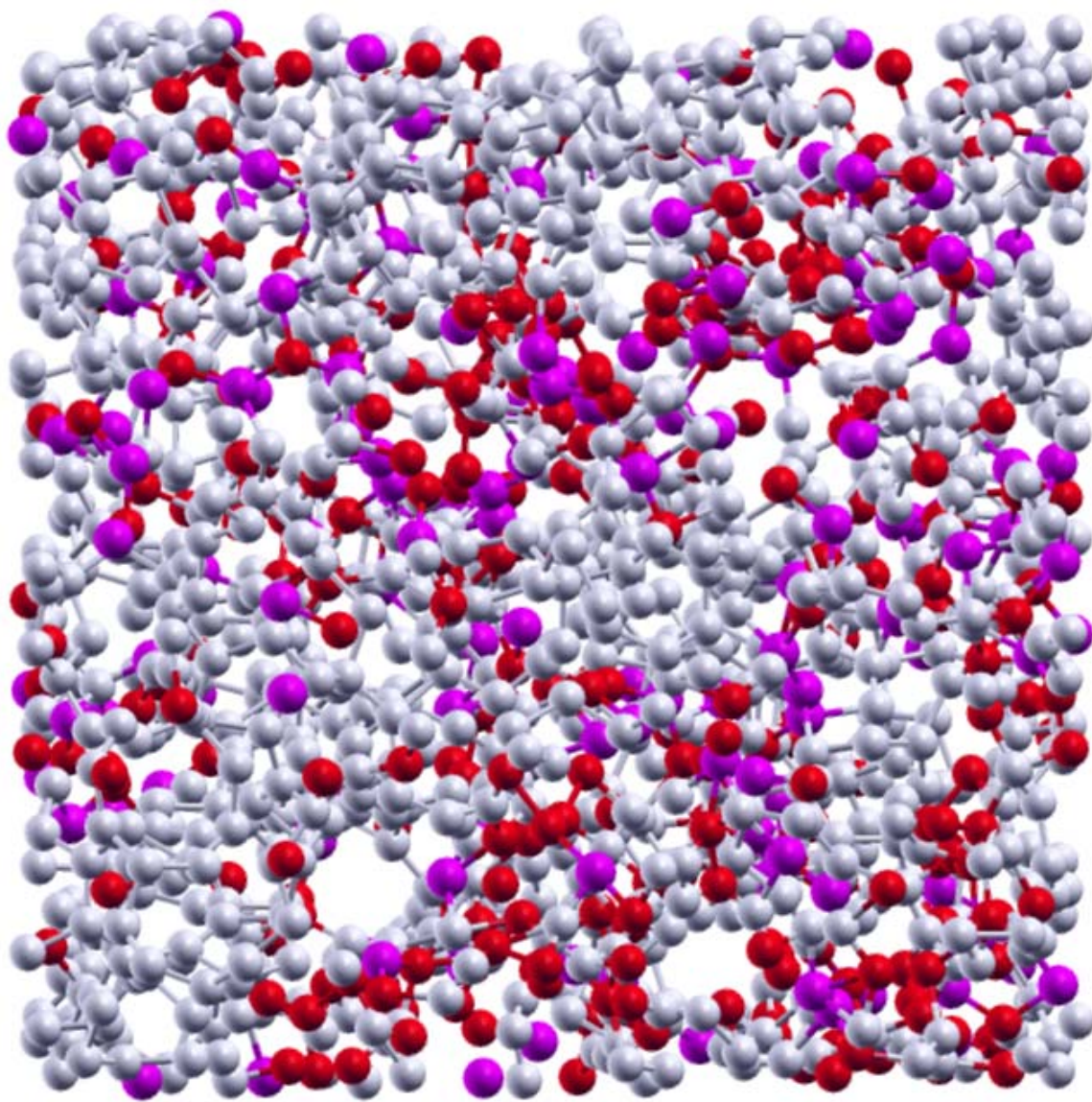


Figure 5.61. Computed structure of GeAs_2Se_7 glass.

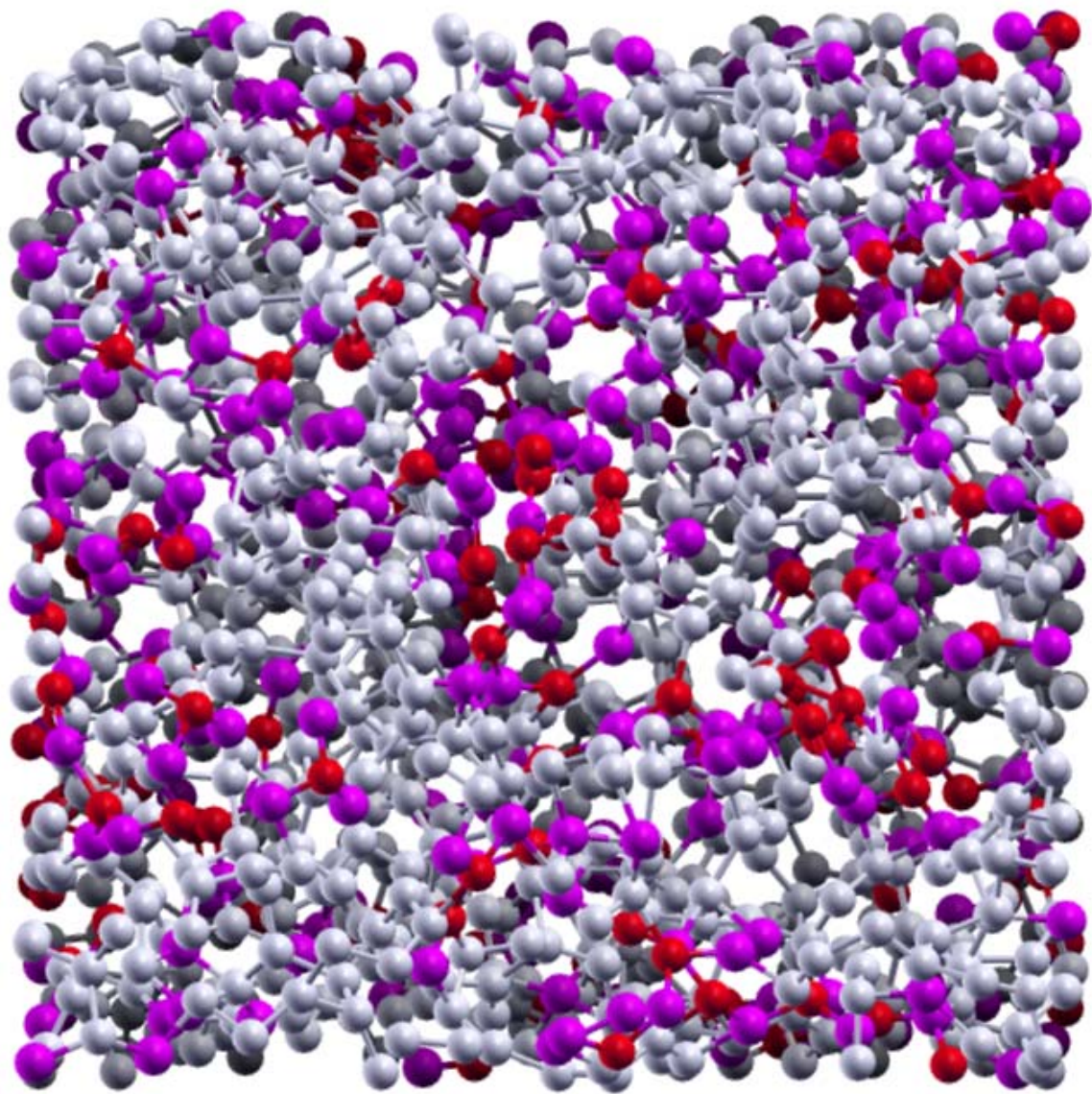


Figure 5.62. Computed structure of Ge_2AsSe_7 glass.

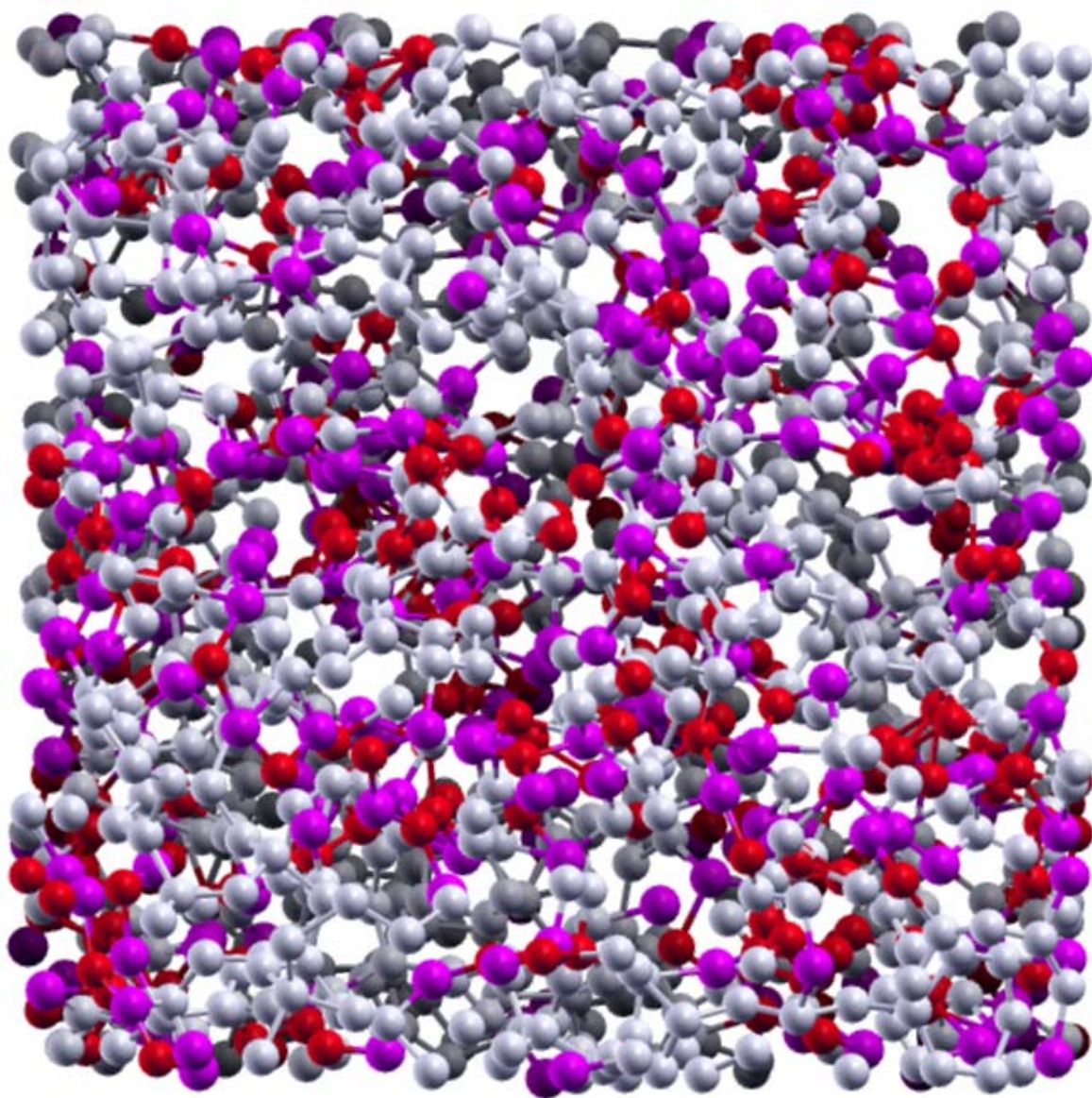


Figure 5.63. Computed structure of $\text{Ge}_2\text{As}_2\text{Se}_6$ glass.

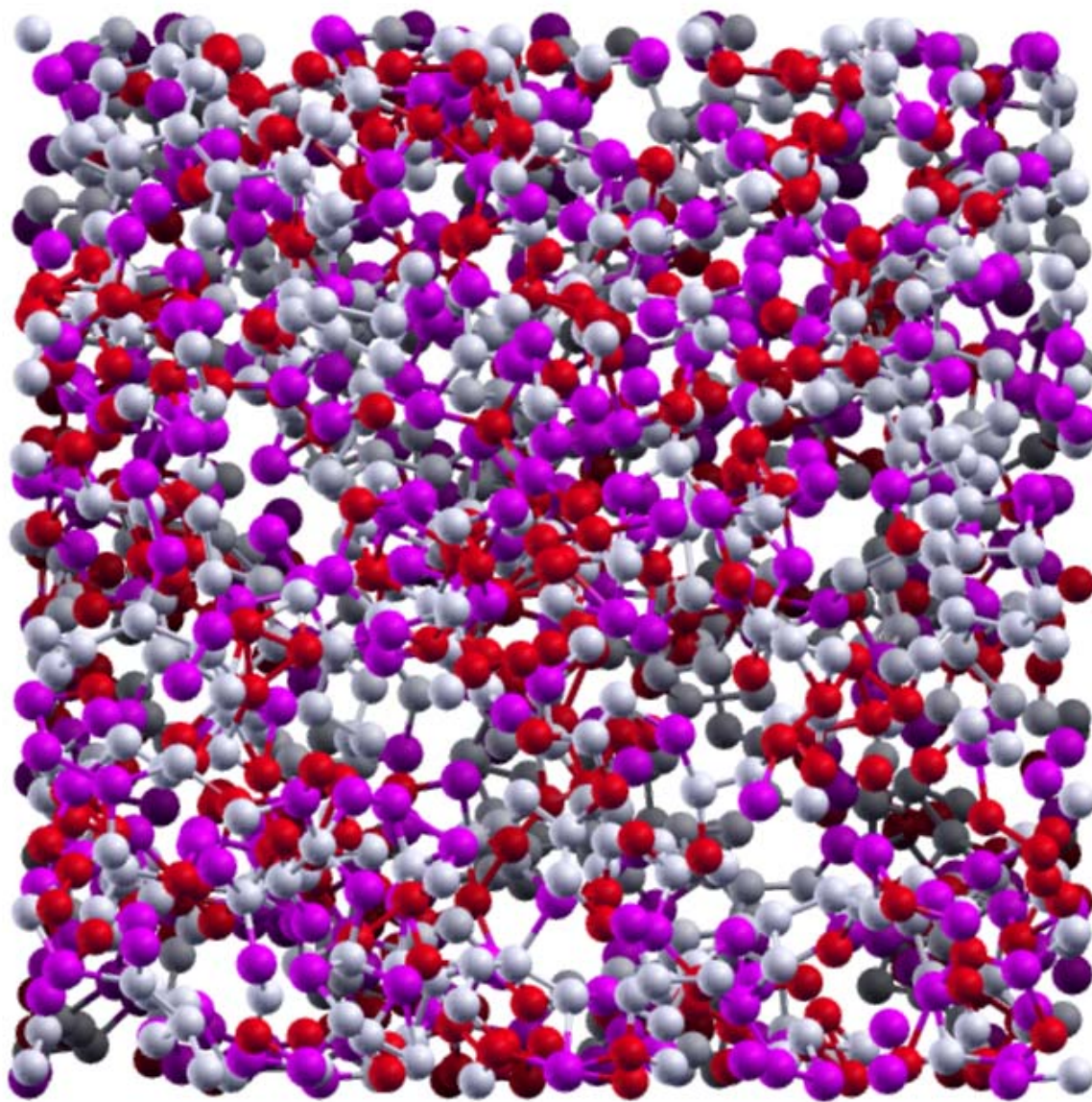


Figure 5.64. Computed structure of $\text{Ge}_4\text{As}_4\text{Se}_7$ glass.

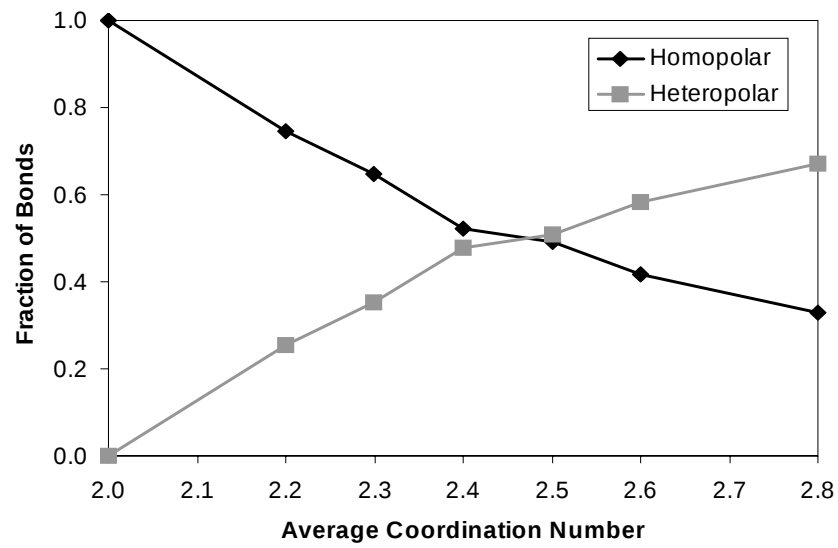


Figure 5.65. Fraction of homopolar and heteropolar bonds in Ge-As-Se glasses as a function of average coordination number.

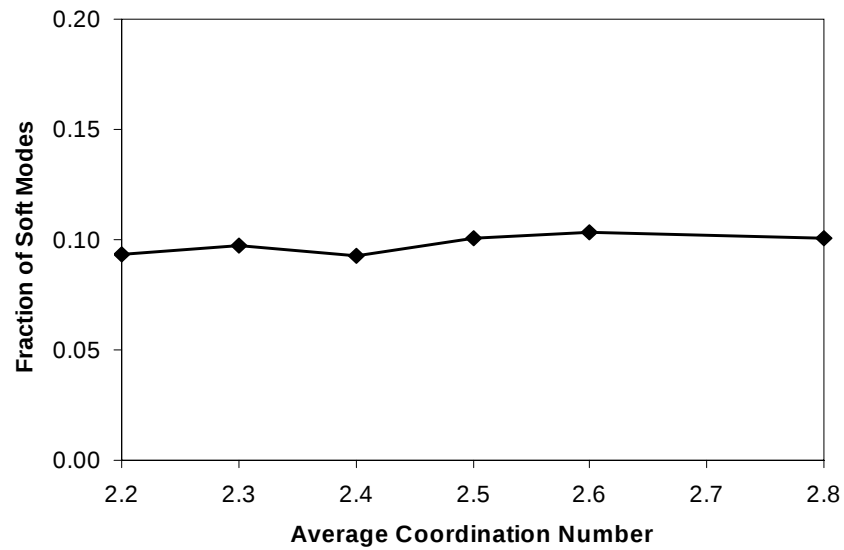


Figure 5.66. Fraction of soft modes in Ge-As-Se glass as a function of the ideal $\langle m \rangle$.

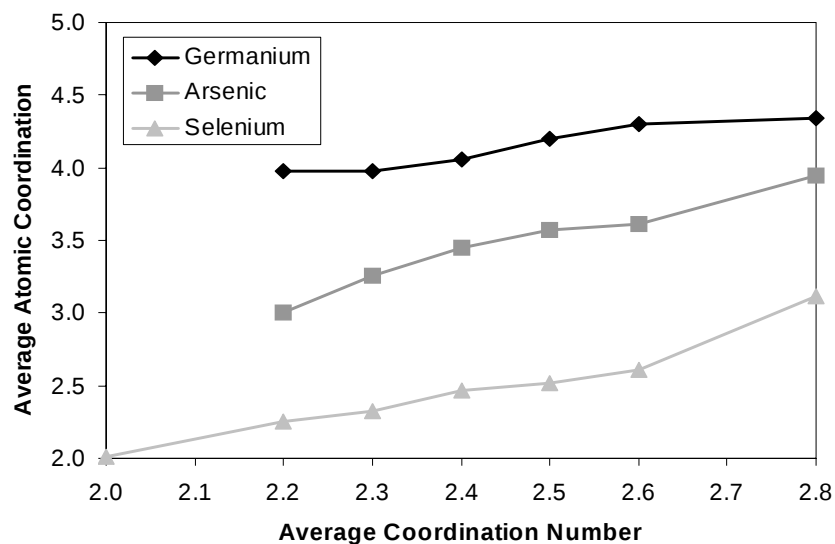


Figure 5.67. Average coordinations of selenium, arsenic, and germanium atoms in Ge-As-Se glasses as a function of the ideal $\langle m \rangle$.

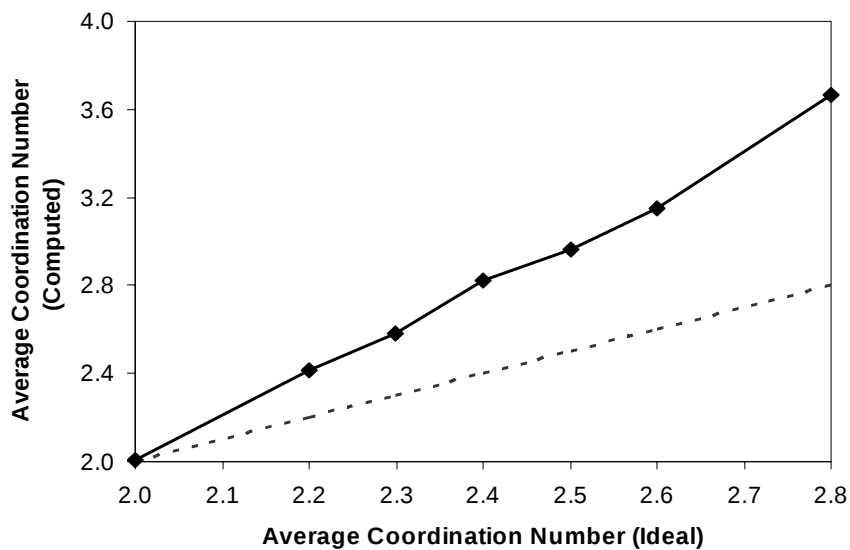


Figure 5.68. Computed versus ideal average coordination numbers for Ge-As-Se glasses. The dashed line shows the nominal case.

5.7 Conclusions

We have performed atomistic Monte Carlo simulations of chalcogenide glasses using our *ab initio* interatomic potentials from Part I. We have successfully reproduced the two-coordinated chain structure of chalcogen glasses. Heterogeneous $\text{Se}_x\text{Te}_{1-x}$ glasses are found to be highly phase separated at the chain level in the regime of $x > 0.2$.

Our multiscale modeling technique is able to capture defect structures in GeSe_2 not previously found with traditional DFT simulations. The scaling of soft modes with respect to average coordination number $\langle m \rangle$ in the bulk glasses provides evidence for a rigidity percolation threshold at $\langle m \rangle = 2.4$. Furthermore, nanoindentation simulations on Ge-Se glass surfaces display critical plastic behavior at $\langle m \rangle = 2.4$. These results give support to the Phillips model of topological constraints for the Ge-Se, which uses counting arguments to predict a rigidity percolation threshold at an average coordination number of $\langle m \rangle = 2.4$.

The binary As-Se system shows a strong preference for chemical ordering. We have found evidence for a rigidity percolation threshold in the regime of $2.3 < \langle m \rangle < 2.4$ for this system.

The ternary Ge-As-Se system has a rigid structure, even with an ideal average coordination number as low as $\langle m \rangle = 2.2$. This result underscores the importance of considering actual average coordination numbers when computing a rigidity percolation threshold, and not strictly relying on their ideal values, since ideal coordination numbers do not necessarily capture the detailed structural features of the glass.

Part III

Energy Landscapes and the Glass Transition

Chapter 6

Introduction to the Glass Transition

From windows and lenses to light bulbs and optical fiber, glass has had a profound positive impact on society. While our scientific understanding of glass has grown immensely in the past century,⁶⁶ the true nature of the glassy state still remains mysterious. It is well-known that the structure and properties of glass depend strongly on both composition and thermal history, but there is yet to be any rigorous physical model explaining this behavior and offering the ability to compute glass properties from fundamental physics.

In this chapter, we discuss the concept of the glass transition and how it governs the experimentally observed properties of glass. We then review several phenomenological, thermodynamic, and kinetic models of the glass transition that each offer important insights into the nature of glass. While none of these models offers a complete picture of the glass transition, they address different aspects of the problem that can be used to construct a

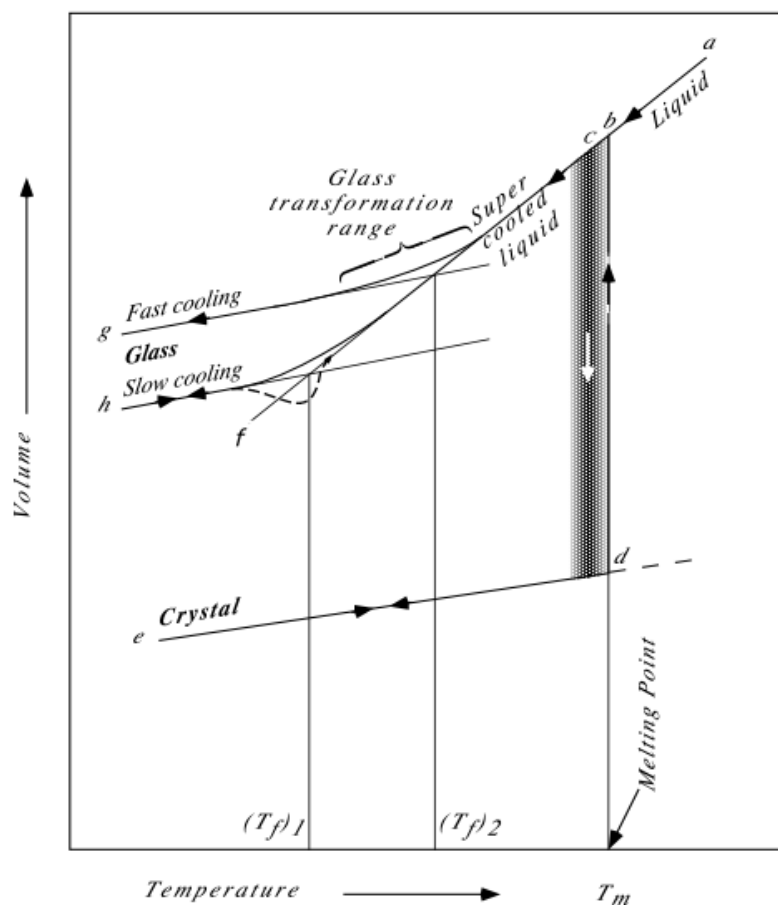


Figure 6.1. The volume-temperature diagram for a glass-forming liquid. Reproduced with permission from Varshneya.⁶⁶

more comprehensive understanding of the glassy state.

6.1 The Glass Transition

Perhaps the most ubiquitous figure in all of glass science is the volume-temperature (V - T) diagram depicted in Figure 6.1. Consider an equilibrium liquid at point a in the diagram. Upon cooling, the volume of the liquid generally decreases along the path abc . Point b corresponds to the melting temperature T_m of the corresponding crystal. At this

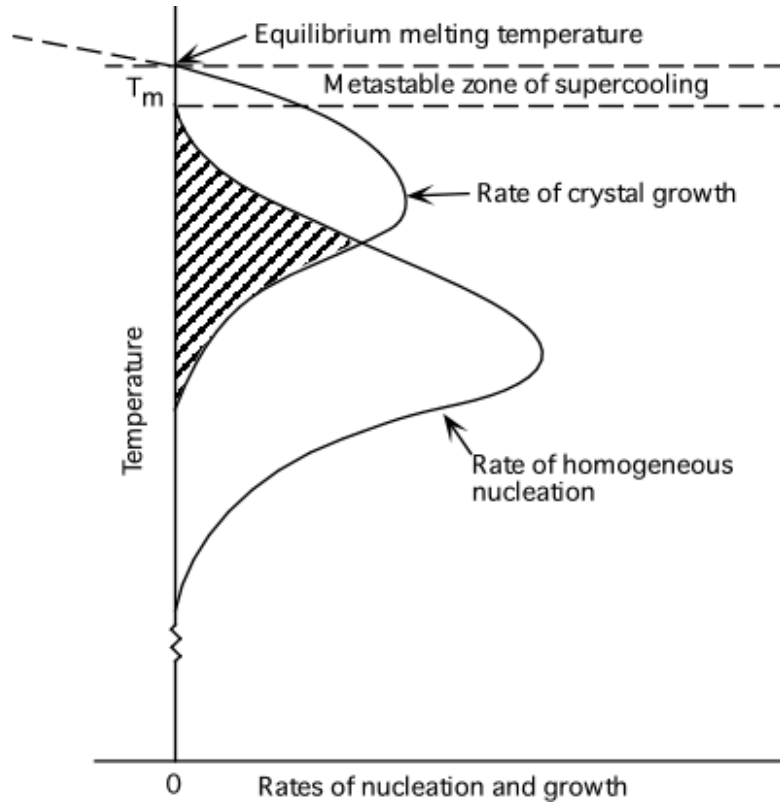


Figure 6.2. Nucleation and crystal growth rates with respect to temperature. Reproduced with permission from Varshneya.⁶⁶

point, the liquid exhibits an infinitesimally small number of crystal nuclei. The degree of crystallization is governed by nucleation and crystal growth rates in the liquid. In this context, a “nucleus” refers to a precursor to a crystal that lacks a recognizable growth pattern. As shown in Figure 6.2, the rates of nucleation and crystal growth are both zero at T_m and in the limit of low temperature. The maximum nucleation and crystal growth rates occur slightly below T_m , corresponding to point c in Figure 6.1. If crystallization occurs, the system undergoes a phase change from point c to the crystal line in the V - T diagram. Subsequent cooling of the crystal generally results in a decrease in volume along the path de .

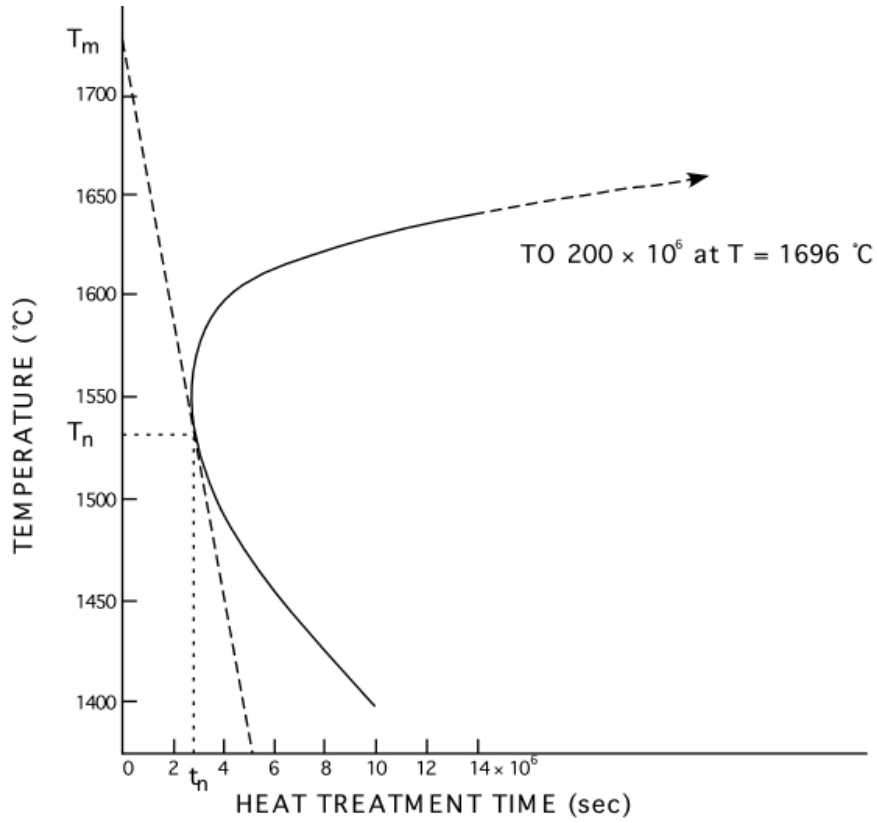


Figure 6.3. Time-temperature-transformation (T - T - T) diagram for silica using a crystal volume fraction of 10^{-6} . Reproduced with permission from Varshneya.⁶⁶

The shaded region around point c in Figure 6.1 corresponds to the temperature region where perceptible crystallization can occur. If a liquid is cooled quickly enough through this temperature range to avoid a phase change, it moves into the “supercooled liquid” state along the path bcf . The minimum cooling rate required to avoid crystallization can be determined using a time-temperature-transformation (T - T - T) diagram, as depicted in Figure 6.3. The solid “transformation” curve in this figure represents the locus of all points in the temperature-time plane which yield a given crystal concentration (typically 10^{-6} volume fraction) which serves as a threshold for crystal detection. Given a liquid at

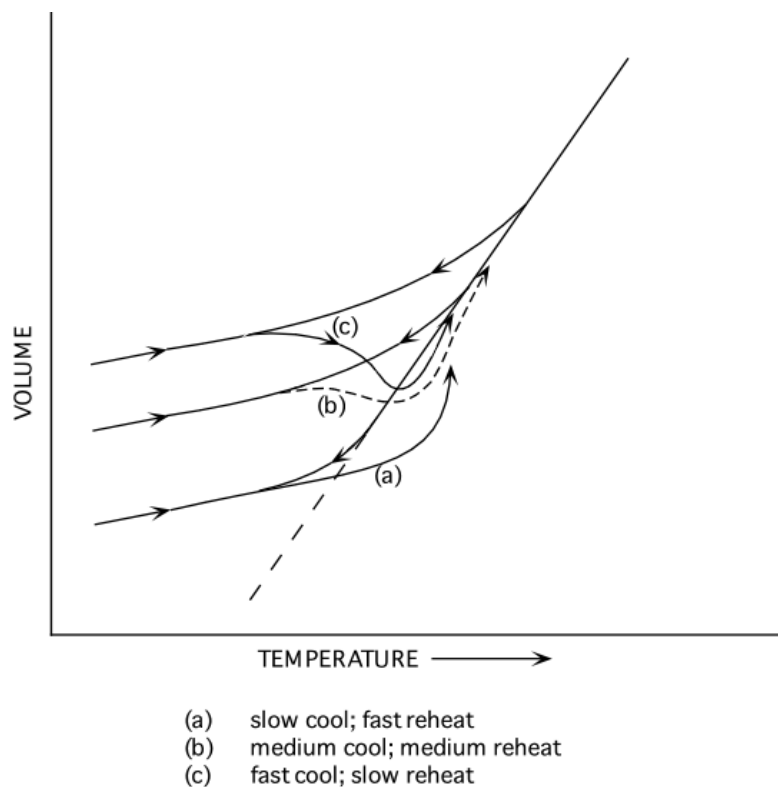


Figure 6.4. Various glass reheating curves. Reproduced with permission from Varshneya.⁶⁶

T_m , the minimum cooling rate to avoid crystallization is determined by the slope of the line which just touches the transformation curve (the dashed line in Figure 6.3).

As a supercooled liquid continues to cool, the molecular motions slow down sufficiently such that the system departs from its straight-line cooling behavior. In other words, the molecules do not have sufficient time to rearrange themselves into the volume characteristic of that temperature and pressure. (Recall that the thermodynamic equation of state for a closed system at equilibrium is defined in terms of any two of V , P , and T .) Further cooling results in a gradual solidification of the system and a return to straight-line cooling behavior in the V - T diagram. The resulting material is a glass. Glass is remarkable in that

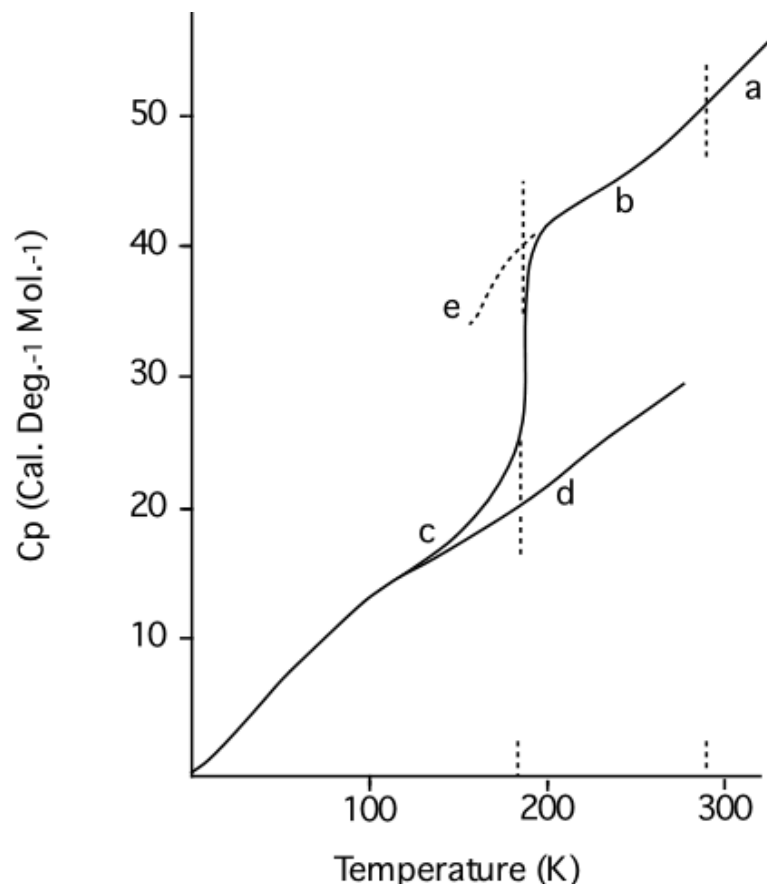


Figure 6.5. Heat capacity of glycerol: (a) liquid, (b) supercooled liquid, (c) glass, (d) crystal, and (e) very slowly cooled supercooled liquid. Reproduced with permission from Varshneya.⁶⁶

it has a liquid-like structure but with solid-like behavior. As shown in Figure 6.1, the final volume of a glass depends on the cooling rate. A faster cooling rate generally results in a higher volume since the molecules are given less time to relax into a lower energy structure before the onset of viscous arrest.

The smooth curve between the supercooled liquid and glassy regions in Figure 6.1 is termed the “glass transition” or “glass transformation” range. It should be emphasized that the transition from the supercooled liquid to glassy states does not occur at a single, well-

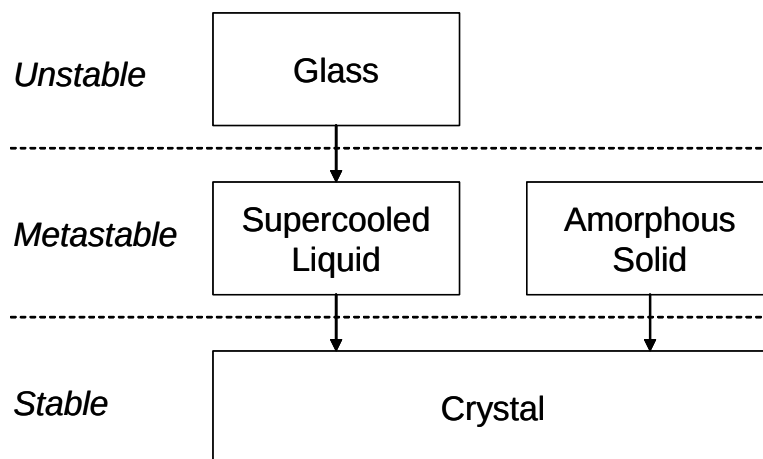


Figure 6.6. Schematic diagram illustrating relative thermodynamic stability.

defined temperature. Rather, the change is gradual and occurs over a range of temperatures. This temperature range depends on both the material under study and the particular cooling path. In other words, glass transition range behavior, and hence the properties of the final glass itself, depend on both composition and thermal history.

Another interesting behavior of glass is that it never retraces its cooling path in the transition range upon reheating. Figure 6.4 shows a variety of reheating curves for different cooling and reheating rates; a quickly cooled glass can actually show a decrease in volume as it is reheated through the transition range.

The glass transition is not a phase transition in the thermodynamic sense. Whereas the crystallization of a liquid results in a discontinuity in first-order thermodynamic variables (such as volume), there is no such discontinuity in the case of a glass transition. Instead, the glass transition often involves a rather sharp change in second-order thermodynamic variables such as heat capacity and thermal expansion coefficient. Figure 6.5 shows the heat capacity of glycerol as it undergoes a glass transition. This change in heat capac-

ity is dramatic, but still not discontinuous. This observation has led some researchers to postulate an “ideal glass transition,” in which a system undergoes a discontinuity in second-order thermodynamic variables. Such an ideal glass transition has not been observed in reality, but only in theoretical or computational studies.

Glass is not an equilibrium state of matter in the statistical mechanical sense. In fact, the only reason we observe the existence of glass at all is that the relaxation dynamics in glass are much slower than our observation time. While glass appears as a rigid, solid material to us humans, on a geologic time scale it is actually relaxing toward the supercooled liquid state. Hence, glass is unstable with respect to the supercooled liquid state. The supercooled liquid is, in turn, metastable with respect to the equilibrium crystal.

Finally, we should comment on the difference between a glass and an amorphous solid. Both materials are noncrystalline, but whereas a glass is continuously connected to the liquid state, an amorphous solid will crystallize upon reheating without undergoing a glass transition.⁶⁷ For example, amorphous silicon prepared by vapor deposition crystallizes directly upon reheating. Interestingly, glassy silicon has not yet been experimentally realized: liquid silicon is 12-coordinated and always crystallizes on cooling, even for the greatest experimentally realizable cooling rates. Figure 6.6 illustrates the relative stability of the glassy, supercooled liquid, amorphous, and crystalline states. In this chapter we are only concerned with glasses and supercooled liquids, not amorphous solids.

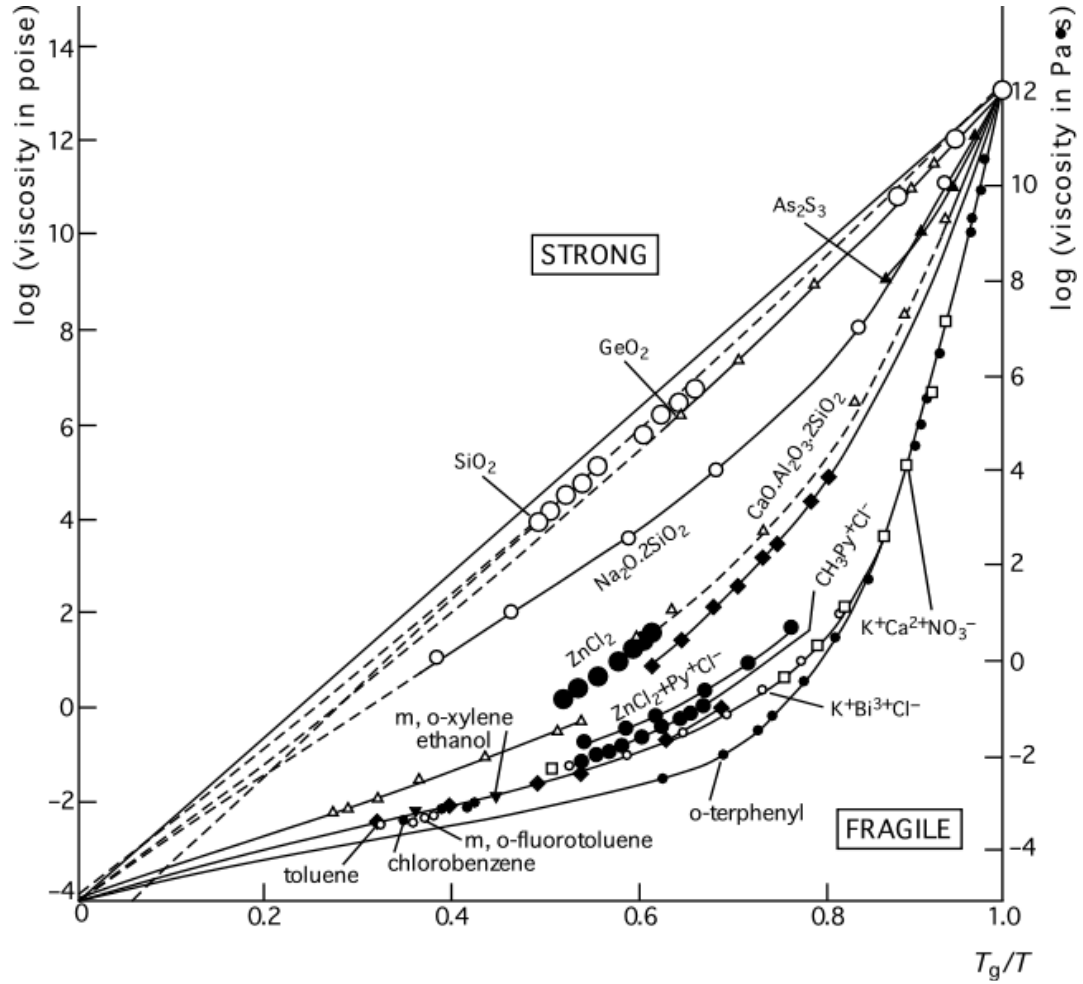


Figure 6.7. Variation of viscosity with normalized inverse temperature T_g/T for strong and fragile liquids. Reproduced with permission from Varshneya.⁶⁶

6.2 Strong and Fragile Liquids

It is useful to classify glass-forming liquids as either “strong” or “fragile,” depending on their observed dependence of viscosity on temperature. According to Angell’s criterion,^{86–89} strong liquids exhibit a behavior that is close to the Arrhenius form,

$$\eta = \eta_0 \exp \left(\frac{\Delta H}{kT} \right), \quad (6.1)$$

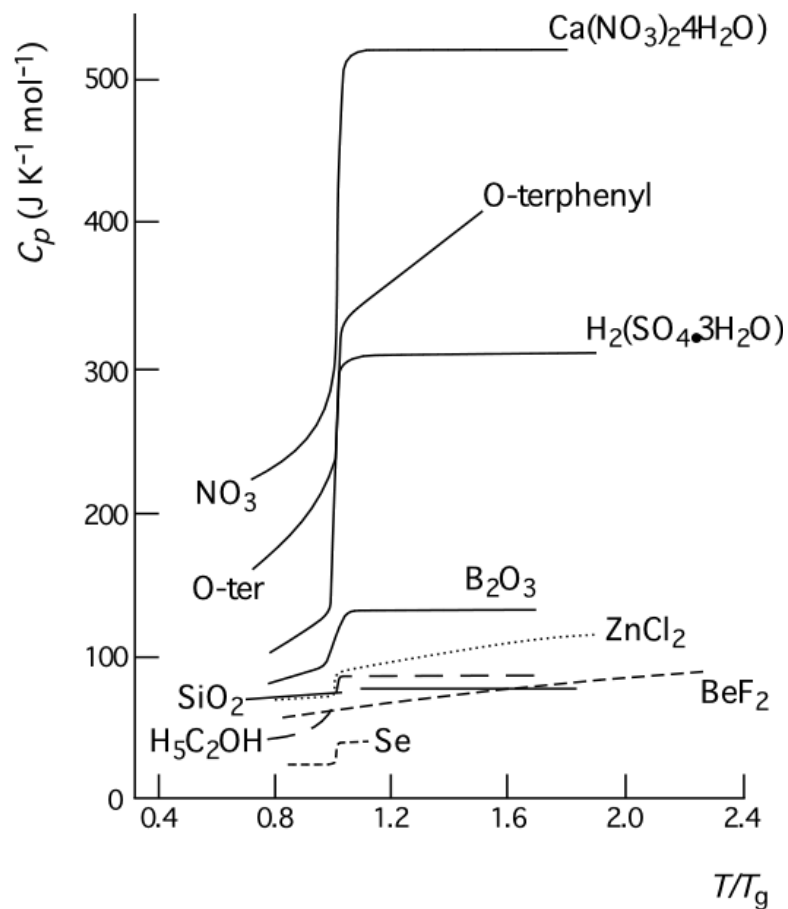


Figure 6.8. Heat capacity as a function of normalized temperature, T/T_g , for various strong and fragile liquids. Reproduced with permission from Varshneya.⁶⁶

where ΔH is an activation barrier to flow, k is Boltzmann's constant, T is temperature, and η_0 is a constant. When the logarithm of viscosity is plotted as a function of inverse temperature, as in Figure 6.7, strong liquids will have a near-straight-line relationship. Examples of strong liquids include silica (SiO_2) and germania (GeO_2).

Fragile liquids, on the other hand, exhibit a large departure from this straight-line relationship. In this case, the viscosity-temperature relationship can often be described by

the Vogel-Fulcher-Tamman (VFT) relation,

$$\eta = \eta_0 \exp \left[\frac{\Delta H}{k(T - T_0)} \right], \quad (6.2)$$

where T_0 is a constant. Examples of fragile liquids include *o*-terphenyl, heavy metal halides, and calcium aluminosilicates. The difference in behavior between strong and fragile liquids is related to allowable relaxation modes of the liquids at different temperatures. Understanding the details of these relaxation modes is a key consideration in modeling glass transition range behavior, as we discuss later in this chapter.

The magnitude of the change in second-order thermodynamic variables during the glass transition is often correlated to the fragility of the glass-forming liquid. Figure 6.8 shows that fragile liquids experience a much greater change in heat capacity during the glass transition than strong liquids.

6.3 The Kauzmann Paradox

In a landmark 1948 paper, Kauzmann¹⁴⁵ plotted the difference in configurational entropy between several supercooled liquids and their corresponding crystalline states. He extrapolated the curves to low temperatures, such as shown in Figure 6.9 for glycerol, and found that the entropy difference becomes zero at a finite temperature T_K , the Kauzmann temperature. Continued extrapolation below T_K would yield negative configurational entropy for the supercooled liquid, in violation of the Third Law of Thermodynamics. Examples of this so-called “Kauzmann paradox” are shown in Figure 6.10.

Kauzmann himself proposed a resolution to this paradox, arguing that the energy

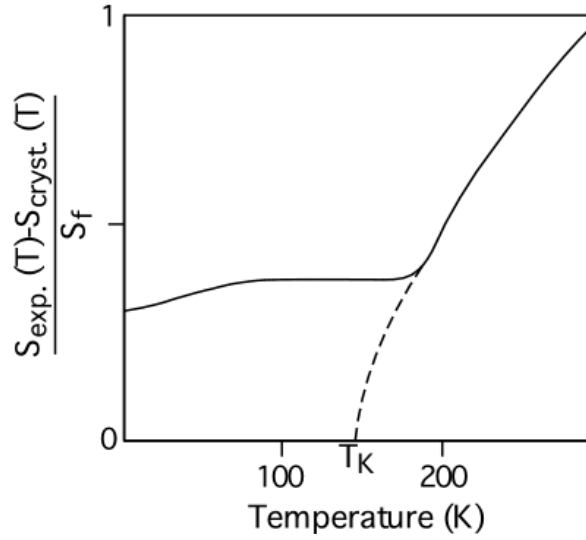


Figure 6.9. Entropy of supercooled and glassy glycerol relative to that of the crystal and normalized to the entropy of fusion S_f . Reproduced with permission from Varshneya.⁶⁶

barrier to crystallization must decrease to the same order as the thermal energy. In this way crystallization would be inevitable at low temperatures, and the issue of negative entropy would be completely meaningless. Figure 6.11 illustrates this point of view in terms of total configurational plus vibrational entropy. The entropy of an infinitely slowly cooled liquid would meet that of the crystalline state at T_K and then follow it down to absolute zero.

The resolution of the Kauzmann paradox is intimately connected to an understanding of the thermodynamics of the glass transition, and forced crystallization is just one possible explanation. In Section 6.5 we will summarize other explanations provided by different thermodynamic models of the glass transition.

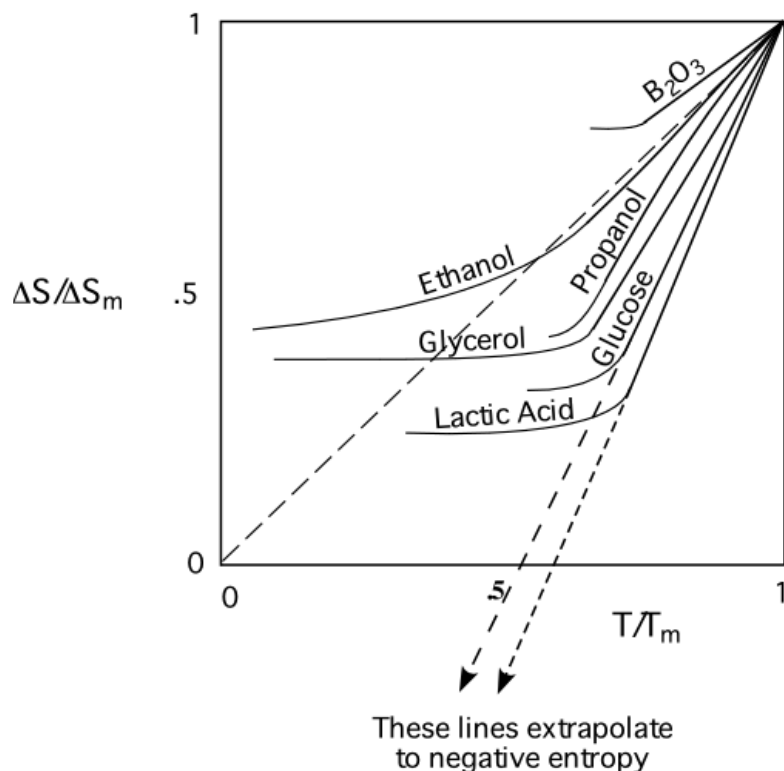


Figure 6.10. Examples of the Kauzmann paradox, where supercooled liquid entropies apparently extrapolate to negative values at low temperature. Reproduced with permission from Varshneya.⁶⁶

6.4 Phenomenological Models

Mathematical models of physical phenomena are classified under many categories, including physical (deterministic or stochastic), empirical, and phenomenological models. The first category usually describes physical mechanisms that are fairly well understood. On the other hand, empirical models are often statistical fits of observed data that predict the expected trend in the behavior of a system. Many systems and phenomena, including glass transition, are too poorly understood to be cast into a rigorous physical model, either deterministic or stochastic. At the same time, these systems may not lend themselves to

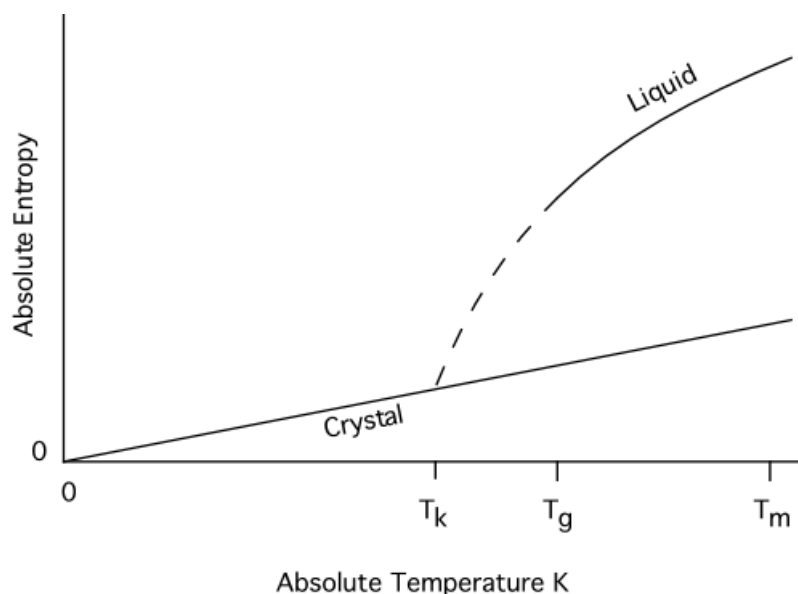


Figure 6.11. Absolute entropy of a supercooled liquid and its corresponding crystal. Reproduced with permission from Varshneya.⁶⁶

statistical extrapolation via empirical models. This is especially true of glass transition range behavior, which is highly dependent on the glass's thermal history. Mathematical models of such systems are often based on a phenomenological approach in order to provide insight into the system's behavior.

Phenomenological models bridge the gap between physical and empirical models, usually by providing a framework that is an analog of the real system. Using a set of control parameters, this framework needs to be tuned to mimic the behavior of the real system. This approach has been used, with some success, to provide kinetic models of glass relaxation. We briefly describe some important developments of this approach to understanding of glass transition behavior in the sections below. It must be stated that an excellent and comprehensive review of such models, as well as related concepts, has been done by Scherer.^{146,147} Other reviews by Mazurin¹⁴⁸ and Rekhson^{149–151} are also worthy

of note here. This section is merely a synthesis of material that may be found in these reviews.

6.4.1 Structural Relaxation and the Fictive Temperature

Phenomenological models of glass transition represent the earliest attempt at providing a mathematical basis for understanding this phenomenon. These models drew their early inspiration from the field of viscoelasticity. This is evident in the usage of the term “structural relaxation” to describe the glass transition phenomenon. This perspective of glass transition considered the glass to undergo a change towards equilibrium much in the same way as a viscoelastic material undergoes stress or strain relaxation. Due to this intimate relation between the two phenomena, and the presence of analogous ideas in their treatment, it is hard to talk exclusively about the structural relaxation of glass without describing the simultaneous work that studied viscoelastic stress relaxation. Nevertheless, we will have to do so in the interest of brevity, especially since we will be summarizing sixty years of previous work.

Possibly the most important concept related to phenomenological modeling of the glass transition is that of a fictive temperature, T_f . Unlike materials in thermodynamic equilibrium, the thermodynamic state of a glass cannot be described in terms of the state variables alone. Hence, Tool¹⁵² proposed the concept of a fictive temperature to allow another degree of freedom by which to describe the nonequilibrium nature of the system.

Tool’s definition of a fictive temperature relates to the viscous arrest of long-range molecular motion during the cooling of a glass-forming liquid. This arrest, which happens at temperatures that are high compared to room temperature, leads to a glass structure

that is not in equilibrium with its surroundings at a lower temperature. Often, the fictive temperature is defined to be that physical temperature at which the glass structure would be in equilibrium, if brought instantaneously to that temperature. However, this is a little inaccurate. A better definition of fictive temperature is more property-specific and describes the relaxation in the appropriate property of the glass. This is important since different properties relax at different rates during glass transition. The fictive temperature can thus be defined as the temperature from which the glass must be instantaneously quenched to obtain a specific value of the property in question.¹⁴⁶ On the V - T diagram (Figure 6.1), the fictive temperature (T_f) is often represented by the temperature where the extrapolated solid and liquid cooling curves intersect. This value is actually the limiting value that the fictive temperature can attain based on the definition above and is often called the glass transition temperature T_g .¹⁴⁶ The fictive temperature thus decreases from a value equal to the physical temperature when the system is a liquid to the final value of T_g when the system has solidified. In this context, the fictive temperature is not a measurable property, unlike the glass transition temperature. Experimentally, the glass transition temperature is often measured using a differential scanning calorimeter (DSC) or a dilatometer.⁶⁶

On the V - T diagram, the slope of the solid and liquid curves represent the coefficients of volume expansion of the respective states. In the glass transition region, the volume change has an additional component, commonly considered as structural expansion, to that of the solid's (elastic) volume expansion. Taking the volume expansion of glass to be isotropic, Tool¹⁵² described the change in length associated with a change in temperature

as the sum of elastic thermal expansion and structural expansion,

$$\frac{L - L_0}{L_0} = \alpha_g (T - T_0) + \alpha_s (T_f - T_{f,0}), \quad (6.3)$$

where L and L_0 are the instantaneous and initial lengths, α_g is the coefficient of elastic thermal expansion between temperatures T and T_0 in the glassy state, and α_s is a coefficient of structural expansion between fictive temperatures T_f and $T_{f,0}$. If the glass is heated and cooled through a thermal cycle that brings it back to its initial temperature, the elastic expansion vanishes. However, the structure of the glass will have changed, leading to a finite length (and free volume) change.

Tool initially proposed a model of structural relaxation where the rate of approach to equilibrium is proportional to the departure from equilibrium.¹⁵² The relationship of this model to viscoelastic stress relaxation is easy to see:

$$\frac{dT_f}{dt} = \frac{T - T_f}{\tau_p}, \quad (6.4)$$

where τ_p is the characteristic relaxation time of property p .

In this model Tool considered the relaxation time to depend on the viscosity, just as it does in viscoelastic relaxation. Unfortunately this formulation did not fit his data well. Tool therefore suggested,¹⁵³ in effect, that the viscosity was a function of the fictive temperature as well as the physical temperature:

$$\eta = \eta_0 \exp(-AT - BT_f), \quad (6.5)$$

where η_0 , A , and B are constants.

This simple phenomenological model by Tool captures the broad features observed in glass relaxation, but described by only a single fictive temperature T_f . Tool's own data showed that a single T_f description is inadequate in the low temperature region. Following up on this work, Ritland¹⁵⁴ showed the limitations of Tool's approach to calculating fictive temperature. Since the glass transition behavior is represented as a single relaxation process, the Tool model fails to effectively account for the effect of thermal history, as seen by Ritland's famous cross-over experiments comparing quenched versus rate-soaked samples. This aspect of glass relaxation involving multiple relaxation times was demonstrated by Macedo and Napolitano¹⁵⁵ and by Spinner and Napolitano.¹⁵⁶ It took nearly two decades after Tool's initial model for Narayanaswamy to make the next major improvement to a phenomenological model of glass relaxation.

6.4.2 Narayanaswamy Model of Relaxation

Arguably the model of glass relaxation that has the widest application today was proposed by Narayanaswamy in his classic 1971 paper,¹⁵⁷ following a previously published study with Gardon.¹⁵⁸ In this work, Narayanaswamy provided a way to deal with the inherently nonlinear nature of glass structural relaxation that was demonstrated by Napolitano and coworkers.^{155,156} This can be seen in the fact that the structural relaxation response depends on both the magnitude and direction of temperature change (data of Hara and Suetoshi¹⁵⁹). In Narayanaswamy's paper, this is expressed by the relation

$$M_p^*(t, \Delta T) = \frac{p - p_{2,\infty}}{p_{2,0} - p_{2,\infty}} = \frac{T_{fp} - T_2}{T_1 - T_2}, \quad (6.6)$$

where the nonlinearity is accounted for by including ΔT as an argument of the relaxation response function M_p^* . The function M_p^* is normalized to unity at time $t = 0$ and to zero at $t = \infty$; p is the value of a property at any time t corresponding to fictive temperature T_{fp} ; $p_{2,0}$ and $p_{2,\infty}$ represent the initial and long-term property values; and $\Delta T = T_1 - T_2$ represents a step change in temperature. Narayanaswamy hypothesized that the nonlinearity inherent to this process was simply due to the time dependence of the characteristic time for structural relaxation of the property under consideration, τ_p . The dependence on ΔT is removed by taking the limit of the response function as the equilibrium temperature is approached. However, this limit is applicable only in a very small temperature range around the equilibration temperature, thus restricting its usefulness. Mathematically, this is expressed as:

$$M_p(t) = \lim_{\Delta T \rightarrow 0} M_p^*(t, \Delta T). \quad (6.7)$$

Narayanaswamy made some important assumptions, which lie at the heart of the phenomenological nature of the model. These assumptions are:

1. The relaxation process can be expressed as the superposition of multiple relaxation processes, along the lines of the Boltzmann superposition principle in linear viscoelastic formulations.
2. Glass maintains thermorheological simplicity (TRS), i.e., the shape of the response function is independent of the temperature range in which it is applied.
3. The intrinsic relation between the cause and effect of relaxation is linear. The nonlinearity arises due to the dependence of viscosity on structural relaxation as well as

temperature.

4. The fictive temperature related to the relaxation behavior of a given property, T_{fp} , is close to the fictive temperature for viscosity relaxation, $T_{f\eta}$. These two quantities can thus be considered equal.

The nonlinearity was removed by considering a reduced time variable, ξ , such that $M_p(\xi)$ is linear:

$$M_p(\xi) = \frac{p - p_{2,\infty}}{p_{2,0} - p_{2,\infty}} = \frac{T_{fp} - T_2}{T_1 - T_2}. \quad (6.8)$$

In doing this, the earlier constraint around the applicability of $M_p(t)$ in a small temperature range is now removed, and the assumptions listed above essentially allow Equation (6.8) to be applied across any temperature range.

The reduced time, ξ , is given by the expression

$$\xi = \int_0^t \phi[T, T_{fp}(t')] dt', \quad (6.9)$$

where

$$\phi[T, T_{fp}(t)] = \frac{\eta_B}{\eta}. \quad (6.10)$$

Here, ϕ is a normalized shift function that relates the viscosity at the current time t to a reference viscosity η_B .

Invoking Tool's phenomenological approach, Narayanaswamy rewrote Tool's ear-

lier expression for viscosity in a more familiar Arrhenius form:

$$\ln \left(\frac{\eta_B}{\eta} \right) = \left[-x \frac{\Delta H}{RT} - (1-x) \frac{\Delta H}{RT_{fp}} \right], \quad (6.11)$$

where ΔH is the activation barrier to relaxation, R is the gas constant, and the parameter x needs to be adjusted to match experimental data. Thus, the viscosity is linked to the structural relaxation, as well as to the temperature. This expression has no theoretical justification, and it hence adds to the core of the phenomenological nature of the model.

With these expressions in place, the response of a property p to a change in temperature can be expressed as

$$p(t) - p(0) = p(0) \left[\alpha_{pl} (T - T_0) - \alpha_{ps} \int_0^\xi M_p(\xi - \xi') \frac{dt}{d\xi'} d\xi' \right], \quad (6.12)$$

where α_{pl} is the coefficient of property change in the liquid state and $\alpha_{ps} = \alpha_{pl} - \alpha_{pg}$, α_{pg} being the coefficient of property change in the glassy state. The property response depends on two terms: the first term is the equilibrium response of the property after complete relaxation, and the second term is the instantaneous contribution due to incomplete relaxation. The integral expression in the second term allows the Narayanaswamy model to capture memory efforts during structural relaxation.

Applying Equation (6.12) to the change in fictive temperature during relaxation, we obtain

$$T_{fp} = T + \int_{\xi(T)}^{\xi(T_0)} M_p(\xi - \xi') \frac{dt}{d\xi'} d\xi' \quad (6.13)$$

Thus, the fictive temperature is expressed as the sum of the physical temperature and the

part of ΔT that is remembered in the glass structure. Substituting Equation (6.13) for the memory integral in Equation (6.12), we regain the property-dependent definition of a fictive temperature:

$$p(t) - p(0) = p(0) [\alpha_{pl}(T_{fp} - T_0) + \alpha_{pg}(T - T_{fp})], \quad (6.14)$$

i.e., the property changes as would a liquid from T_0 to T_{fp} and a solid from T_{fp} to T . For a change in free volume, this would correspond to an elastic thermal expansion in two stages (liquid and solid).

In order to relate Narayanaswamy's formulation to that of Tool, we can consider some specific forms of the response function M_p . When $M_p = 0$, as is the case for instantaneous relaxation in the liquid state, $T_f = T$. When the glass is instantaneously quenched from a liquid state at a temperature T_0 to a final state $T_1 \ll T_g$, $M_p = 1$ and $T_f = T_0$. If we assume M_p to represent a single relaxation process, then we get

$$M_p(\xi) = \exp\left(-\frac{\xi}{\tau_{pr}}\right), \quad (6.15)$$

where τ_{pr} represents τ_p in reduced time.

Thus, Equation (6.13) becomes

$$T_{fp} = T - \int_0^\xi \exp\left(-\frac{\xi - \xi'}{\tau_{pr}}\right) \frac{dt}{d\xi'} d\xi'. \quad (6.16)$$

Taking the derivative with respect to ξ , we obtain

$$\frac{dT_{fp}}{d\xi} = \frac{dT}{d\xi} - \frac{dT}{d\xi} + \frac{1}{\tau_{pr}} \int_0^\xi \exp\left(-\frac{\xi - \xi'}{\tau_{pr}}\right) \frac{dt}{d\xi'} d\xi'. \quad (6.17)$$

Substituting Equation (6.12) into Equation (6.17), we obtain

$$\frac{dT_{fp}}{d\xi} = \frac{T - T_{fp}}{\tau_{pr}}. \quad (6.18)$$

Since

$$d\xi = \frac{\tau_p}{\tau_{pr}} dt, \quad (6.19)$$

we have

$$\frac{dT_{fp}}{dt} = \frac{T - T_{fp}}{\tau_p}. \quad (6.20)$$

This is exactly the same expression that Tool proposed¹⁵² for structural relaxation. Thus, the Narayanaswamy model is a generalization of Tool's formulation that accounts for multiple relaxation phenomena occurring simultaneously. In Narayanaswamy's model, the fictive temperature is often represented as a weighted average of many different fictive temperature components, each obeying Equation (6.20):

$$T_{fp} = \sum_i w_i T_{fp,i}. \quad (6.21)$$

The weighting factors w_i and the individual relaxation times $\tau_{p,i}$ need to be fitted to match experimental data, in addition to the previously mentioned parameter x for viscosity weighting. Once this parameterization has been done for a certain glass composition, the model

can successfully capture the complexities of glass relaxation.

The success of Narayanaswamy's model is evident from its extensive use by many researchers in studying glass relaxation.¹⁴⁸ The model can explain the cross-over phenomenon seen in Ritland's experiments,¹⁵⁴ as well as other hysteresis effects in structural relaxation.

The success of the Narayanaswamy-Tool approach lies partly in the phenomenological description of viscosity, as a weighted sum of Arrhenius contributions from the temperature and the fictive temperature (Equation (6.11)). Although this has no theoretical basis, it accurately fits both the case of equilibrium, when $x = 1$, as well as other experimental data from many studies.¹⁴⁸ Some studies ascribing thermodynamic descriptions to the variation in viscosity show a qualitative agreement with the phenomenological form given above. For example, Macedo and Litovitz¹⁶⁰ propose a form of viscosity given by

$$\eta = \eta_0 \exp \left(\gamma \frac{V_c}{V_f} + \frac{Q}{RT} \right), \quad (6.22)$$

where V_c is the core or occupied volume of the atoms, V_f is the free volume, Q is an activation energy, and η_0 and γ are constants. This uses a combination of the free volume and Arrhenius approaches. Scherer¹⁶¹ proposed that the free volume can be expressed in terms of the fictive temperature such that

$$\eta = \eta_0 \exp \left(\frac{\gamma}{\int_{T_1}^{T_{fv}} \beta_s dT} + \frac{Q}{RT} \right), \quad (6.23)$$

where $\beta_s = \beta_l - \beta_g$, and β_l and β_g are the volume thermal expansion coefficients of the

liquid and glass, respectively.

In addition, a form of Equation (6.11) has been suggested by Mazurin¹⁴⁶ using an empirical fit to data:

$$\eta = \eta_0 \exp \left[\frac{A}{T_{fp} - T_0} + \frac{Q}{R} \left(\frac{1}{T} - \frac{1}{T_{fp}} \right) \right], \quad (6.24)$$

where A is a constant. At equilibrium, this reduces to the familiar VFT expression for viscosity in Equation (6.2).

In these expressions, an attempt has been made to link viscosity to both the temperature and the glass structure using thermodynamic principles. Their resulting form is very close to Tool's assumption which had no theoretical basis. Thus, the judicious choice of the form of the viscosity expression by Tool, and later by Narayanaswamy, allowed the phenomenological model to qualitatively explain the physics of structural relaxation. In this brief review, we have omitted various studies that relate to different forms of the response function M_p . Various examples include the Kohlrausch-Williams-Watts stretched exponential expression, the Prony series, and others.¹⁴⁶ The form of the response function does not interfere with the basic formulation of Narayanaswamy. We also omit work challenging Narayanaswamy's assumption on thermorheological simplicity,^{162, 163} which may be important in eventually improving the phenomenological formulation. The topics we have omitted are reviewed elsewhere.¹⁴⁶

6.5 Thermodynamic Models

Thermodynamic models of the glass transition offer the opportunity to discover and understand the underlying physical principles and mechanisms involved in liquid supercooling and vitrification. In this section, we describe several such models and discuss their inherent advantages and shortcomings.

6.5.1 Free Volume Model

Perhaps the simplest thermodynamic model of the glass transition is the free volume model of Turnbull and Cohen¹⁶⁴ and of Cohen and Grest.¹⁶⁵ The underlying idea of this model is that the increase of the viscosity of a liquid as it is supercooled is a direct result of a decrease in its free volume. Here, “free volume” is defined as an excess volume of the supercooled liquid or glass with respect to the equilibrium crystal state. For a relaxation time τ and available time Δt , the volume V of a system may be found via

$$\frac{V - V_c}{V_i - V_c} = \exp(-\Delta t/\tau), \quad (6.25)$$

where V_i is the initial volume of the system and V_c is the volume of the equilibrium crystal. The relaxation time $\tau(V_f)$ is a function of the free volume V_f of the system and is written

$$\tau(V_f) = \tau_0 \exp\left(\frac{V_0}{V_f}\right), \quad (6.26)$$

where τ_0 and V_0 are constants. The free volume-dependent volume viscosity $\eta_V(V_f)$ of the system is given by

$$\eta_V(V_f) = \frac{\tau(V_f)}{\kappa}, \quad (6.27)$$

where κ is isothermal compressibility.

Given a cooling rate of $B = \Delta T/\Delta t$, Equation (6.25) becomes

$$\frac{V - V_c}{V_i - V_c} = \exp\left(-\frac{\Delta T}{B\kappa\eta_V(V_f)}\right) \quad (6.28)$$

We may approximate $V_i - V_c$ by

$$V_i - V_c \approx V_c\beta_f\Delta T, \quad (6.29)$$

where β_f is the thermal expansion coefficient of the free volume (may be the same as $\beta_s = \beta_l - \beta_c$), in order to obtain

$$\frac{V - V_c}{V_c\beta_f\Delta T} = \exp\left(-\frac{\Delta T}{B\kappa\eta_V(V_f)}\right) \quad (6.30)$$

or

$$V = V_c \left[1 + \beta_f\Delta T \exp\left(-\frac{\Delta T}{B\kappa\eta_V(V_f)}\right) \right]. \quad (6.31)$$

In this manner, the model allows for the calculation of the volume of a system as it is cooled or heated through the glass transition.

The free volume model has several major shortcomings, as enumerated by Gupta,¹⁶⁶ that prevent it from providing a correct picture of the glass transition. One serious problem

is that some liquids, such as silica,⁶⁶ water,¹⁶⁷ and lithium acetate,¹⁶⁶ show an increase in free volume when they are cooled in a certain temperature regime;* this is inconsistent with the model, which assumes that free volume always decreases as a liquid is cooled. Also, the free volume model implicitly assumes that V_f has been defined as a function of all relevant state variables and the appropriate constants have been found to obtain the precise relationship between V_f and τ . This may be accomplished using approximate thermodynamic techniques¹⁶⁵ or using an empirical expression valid in a limited phase space.⁶⁶ Thus, the theoretical value of the free volume model is limited.

6.5.2 Gibbs-DiMarzio Model of an Ideal Glass Transition

Gibbs and DiMarzio¹⁶⁹ developed a thermodynamic model that predicts a lower limit to the glass transition temperature for a linear molecular chain polymer, this lower limit corresponding to the Kauzmann temperature for the given material. The Gibbs-DiMarzio model addresses the Kauzmann paradox by predicting an ideal glass transition at the Kauzmann temperature, giving the “ground state” of the glass. This ideal glass transition corresponds to a perfect second-order Ehrenfest transition, leading to discontinuities in heat capacity and other second-order thermodynamic properties. In this section, we provide an overview of the Gibbs-DiMarzio model for the glass transition and discuss some of its inherent limitations.

The Gibbs-DiMarzio model considers a linear, molecular polymer on a fixed lattice in the canonical ensemble. The lattice points may be occupied by either “atoms” or “holes,”

*It may be noted that Shelby¹⁶⁸ has recently objected to this characterization of the silica cooling curve. However, one indisputable example of liquid expansion on cooling is liquid water near its normal freezing point. As water is cooled below 4° C and then supercooled below 0° C, both volume and viscosity increase simultaneously.¹⁶⁷ This is a clear example of where the free volume model breaks down.

where an atom corresponds to one monomer unit and a hole indicates the absence of any monomer at that lattice point. The system consists of n_x polymer chains, each containing x monomer units; the number of holes is designated by n_0 . The total energy of the system is the sum of the intramolecular (polymer) energy and intermolecular (hole) energy. The intramolecular energy is given by

$$E = f\epsilon_2 (x - 3) n_x + (1 - f) \epsilon_1 (x - 3) n_x, \quad (6.32)$$

where ϵ_1 and ϵ_2 are the energies corresponding to different possible bond orientations in the polymer. The first energy, ϵ_1 , corresponds to the primary chain backbone, and the second energy, ϵ_2 , is the “flexed” bond energy; f is the fraction of bonds in the flexed configuration.

The intermolecular energy is proportional to the number of holes in the system and the Van der Waals energy of interaction. The total intermolecular energy is given by

$$\Phi = \frac{1}{2} z' \alpha n_0 S'_x, \quad (6.33)$$

where z' is the coordination number of the “optimal” lattice in amorphous packing, α is the Van der Waals energy per interaction, and S'_x is fraction of non-bonded but nearest neighboring monomers:

$$S'_x = \frac{[(z' - 2) x + 2] n_x}{[(z' - 2) x + 2] n_x + z' n_x}. \quad (6.34)$$

The thermodynamic properties of the system may be calculated using the canonical

partition function,

$$Q = \sum_{\substack{W=1 \\ f, n_0}}^{W=\infty} W(f, n_0) \exp \left[-\frac{(E + \Phi)}{kT} \right] \quad (6.35)$$

$$= \sum_{\substack{W=1 \\ f, n_0}}^{W=\infty} W(f, n_0) \cdot \exp \left[-\frac{[f\epsilon_2(x-3)n_x + (1-f)\epsilon_1(x-3)n_x] + z'\alpha n_0 S'_x/2}{kT} \right], \quad (6.36)$$

where $W(f, n_0)$ is the total number of ways the n_x polymers of length x can be packed onto the lattice of $xn_x + n_0$ sites with f as the fraction of bonds in the flexed configuration.

Assuming an ideal coordination of $z = z'$, W is given by Flory's expression

$$W = \frac{(xn_x + n_0)! z^{xn_x} \left\{ \frac{[(z-2)x+2]n_x + zn_0}{2} \right\}! (z-1)^{n_x} (z-2)^{f(x-3)n_x} [(x-3)n_x]!}{(n_0)! [(xn_x + n_0)z/2]! 2^{xn_x} (n_x)! [(1-f)(x-3)n_x]! [f(x-3)n_x]!}. \quad (6.37)$$

Since Flory's expression may run from 0 to ∞ instead of 1 to ∞ , Gibbs and DiMarzio rewrite the partition function as

$$Q = Q' - Q'', \quad (6.38)$$

where

$$Q' = \sum_{\substack{W=0 \\ f, n_0}}^{W=\infty} W(f, n_0) \exp \left[-\frac{[f\epsilon_2(x-3)n_x + (1-f)\epsilon_1(x-3)n_x] + z\alpha n_0 S_x/2}{kT} \right] \quad (6.39)$$

and

$$Q'' = \sum_{\substack{W=1 \\ W=0 \\ f, n_0}} W(f, n_0) \exp \left[-\frac{[f\epsilon_2(x-3)n_x + (1-f)\epsilon_1(x-3)n_x] + z\alpha n_0 S_x/2}{kT} \right]. \quad (6.40)$$

Values of W less than unity do not correspond to any real states of the system and must therefore be discarded.

Substituting Equation (6.37) into Equation (6.39) and factoring the partition function yields

$$Q' = \left\{ \sum_{n_0} \frac{(xn_x + n_0)! z^{xn_x} \left\{ \frac{[(z-2)x+2]n_x + zn_0}{2} \right\}! (z-1)^{n_x} \exp \left(-\frac{z\alpha n_0 S_x}{kT} \right)}{(n_0)! [(xn_x + n_0)z/2]! 2^{xn_x}} \right\} \times$$

$$\left\{ \sum_f \frac{(z-2)^{f(x-3)n_x} [(x-3)n_x]! \exp \left(-\frac{[f\epsilon_2(x-3)n_x + (1-f)\epsilon_1(x-3)n_x]}{kT} \right)}{(n_x)! [(1-f)(x-3)n_x]! [f(x-3)n_x]!} \right\} \quad (6.41)$$

$$= \mu' \lambda', \quad (6.42)$$

where μ' and λ' represent the factors summed over n_0 and f , respectively. The factor λ' is evaluated by recognizing that each term in the summation is a term of the binomial expansion of $[\exp(-\epsilon_1/kT) + (z-2)\exp(-\epsilon_2/kT)]^{n_x}$ multiplied by $1/(n_x)!$; hence,

$$\lambda' = \frac{[\exp(-\epsilon_1/kT) + (z-2)\exp(-\epsilon_2/kT)]^{n_x}}{(n_x)!}. \quad (6.43)$$

Gibbs and DiMarzio show that the Helmholtz free energy of the system where the maximum degeneracy, $W'_{\max}$, is greater than unity may be approximated by

$$F_{T>T_2} = -kT \ln Q'. \quad (6.44)$$

This corresponds to the regime where μ' and λ' are dominated by single terms containing $n'_{0\max}$ and $f'_{\max}$, respectively. Since the maximum degeneracy, $W'_{\max}$, increases monotonically with temperature, we may state that Equation (6.44) is only valid for systems above some critical temperature, T_2 . The temperature T_2 corresponds to the point where $W'_{\max}$ equals unity. The partition function below T_2 is approximated by the case where $W'_{\max} = 1$, giving

$$F_{T < T_2} = -kT \ln [Q_{\max}(f_{T_2})]. \quad (6.45)$$

The two expressions for Helmholtz free energy in Equations (6.44) and (6.45) are continuous at $T = T_2$. In fact, Gibbs and DiMarzio show that while all “first-order” thermodynamic functions (including entropy, enthalpy, and volume) are described by different analytical forms in the two temperature regimes, they are all continuous at the transition temperature $T = T_2$. However, their first temperature derivatives (the “second-order” thermodynamic functions such as heat capacity and thermal expansion coefficient) are discontinuous at $T = T_2$. Hence, the transition at T_2 corresponds to an ideal second-order thermodynamic transition, i.e., an *ideal glass transition*.

Thus, the Gibbs-DiMarzio model predicts a finite temperature T_2 where all the monomers and holes can only be arranged in one particular configuration. In other words, the configurational entropy becomes zero at T_2 . This critical temperature corresponds exactly to the Kauzmann temperature T_K and represents a lower limit to the glass transition temperature of a system. An infinitely slowly cooled system would thus achieve the “ground state” of amorphous packing at $T = T_2$ and be unable to undergo any further rearrangements of its structure.

The Gibbs-DiMarzio model provides a thermodynamic explanation of the Kauzmann paradox by demonstrating that the configurational entropy of such an infinitely slowly cooled system becomes zero at $T_2 = T_K$. Rather than demanding crystallization at the Kauzmann temperature, the Gibbs-DiMarzio model simply reduces the number of possible atomic arrangements to one. Hence, the configurational energy of a system is zero between the Kauzmann temperature and absolute zero. In accordance with the Third Law of Thermodynamics, the system loses vibrational entropy as it is cooled from $T = T_K$ to $T = 0$.

Of course, ordinarily cooled glasses undergo the glass transition at some temperature greater than T_2 . Hence, no experimentally observable glass transition is an ideal second-order thermodynamic transform as predicted by the Gibbs-DiMarzio model, and in reality there is no sharp discontinuity of second-order thermodynamic variables at the glass transition temperature. Because there is no time variable in the Gibbs-DiMarzio model, it cannot be used to predict realistic glass transition range behavior.

There are several other major shortcomings of the Gibbs-DiMarzio model. The most obvious is that the Gibbs-DiMarzio model uses equilibrium statistical mechanics to describe a system which is certainly not in equilibrium. At the same time, there is no mention of the “true” equilibrium structure of the system, i.e., that of the crystal. There is an implicit assumption in the model that the system will never be able to achieve crystalline order. This brings their conclusions of a “ground state” of amorphous packing and an “ideal glass transition” into serious question.

Perhaps even more troubling is the assumption that the constituent particles and

holes of a system must always occupy discrete sites on fixed lattice. The central argument of Gibbs and DiMarzio rests on this unjustified assumption, which they use to break the partition function into two pieces. The piecewise continuous expression for the partition function leads directly to the discontinuity in second-order thermodynamic variables at $T = T_2$. In this sense, the expression used in the Gibbs-DiMarzio model lacks adequate physical rigor, and its design achieves a desired result, viz., an ideal second-order thermodynamic transition.

Despite its shortcomings, the Gibbs-DiMarzio model does provide for interesting discussion about the nature of a system that would lead to an ideal glass transition. However, the inherent assumptions in the model severely limit both its theoretical and practical applicability to studying the glass transition behavior of a realistic system.

6.5.3 Adam-Gibbs Model of Cooperative Relaxations

According to Gibbs and DiMarzio,¹⁶⁹ the fluidity of a system depends directly on the rate of disappearance of the configurational entropy. A system at the ideal glass transition temperature T_2 has no more configurational entropy to lose, so the system becomes frozen into the “ground state” of amorphous packing. This argument of entropy-dependent flow was subsequently used by Adam and Gibbs¹⁷⁰ to develop an entropy-based theory of structural relaxation that describes the viscosity-temperature relationship of a liquid.

The central assumption of the Adam-Gibbs model is that a liquid consists of a number of regions or subsystems that can cooperatively rearrange. Each region is composed of a group of z molecules or monomers that can rearrange itself independently of its environment in response of an enthalpy fluctuation in the system. As the liquid is

supercooled the configurational entropy of the system is diminished and the size of the cooperatively rearranging subsystems grows progressively larger. When the configurational entropy becomes zero at $T = T_2$, the system consists of just one cooperatively relaxing region; at this point, there is no further freedom for the system to rearrange its structure, and the system has zero fluidity (infinite viscosity).

The Adam-Gibbs model is derived based on the isothermal-isobaric partition function

$$\Delta(z, P, T) = \sum_{E, V} w(z, E, V) \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{PV}{kT}\right), \quad (6.46)$$

where w is the degeneracy of the subsystem with energy E and volume V . The Gibbs free energy of the system is given by $G = -kT \ln \Delta$. If the summation in Equation (6.46) is confined to only those values of E and V that allow a transition, we obtain a “restricted” partition function Δ' and a corresponding Gibbs free energy $G' = -kT \ln \Delta'$. The fraction of subsystems that allow for rearrangement is given by

$$f = \frac{\Delta'}{\Delta} = \exp\left[-\frac{(G' - G)}{kT}\right]. \quad (6.47)$$

The probability of a cooperative transition is proportional to f and may be written as

$$p(T) = A \exp\left(-\frac{z\delta\mu}{kT}\right), \quad (6.48)$$

where A is a frequency factor and $\delta\mu = (G' - G)/z$ is the difference in chemical potential per monomer between rearrangeable and non-rearrangeable subsystems. The average transition

probability is therefore

$$\langle p(T) \rangle = \sum_{z=z^*}^{\infty} A \exp\left(-\frac{z\delta\mu}{kT}\right) \quad (6.49)$$

$$= \frac{A \exp(-z^*\delta\mu/kT)}{1 - \exp(-\delta\mu/kT)} \quad (6.50)$$

$$\approx \langle A \rangle \exp(-z^*\delta\mu/kT), \quad (6.51)$$

where z^* is the lower limit to the sizes of the cooperative regions that have nonzero transition probabilities.

Adam and Gibbs assume that the partition function of the supercooled liquid can be rewritten as the product of independent configurational and vibrational partition functions. The configurational partition function relates to the exploration of the various minima in the potential energy landscape, and the vibrational partition function relates to the thermal vibrations within one of these minima. If we let $\Omega(E_{pot}, V, N)$ equal the number of distinguishable potential energy minima of depth E_{pot} in a system an N -molecule system of volume V , the configurational entropy of the entire system can be written as

$$S_{conf} = k \ln \Omega(E_{pot}, V, N) \approx n s_{conf}, \quad (6.52)$$

where n is the number of cooperatively rearranging regions. Each of these regions is assumed to be of identical size z and contribute s_{conf} to the total configurational entropy of the system. This additivity follows from the assumption that each of the cooperatively rearranging regions is independent of its environment. Since in one mole of molecules there are $n = N_A/z$ independent regions (N_A equals Avogadro's number), the minimum size of

the cooperatively rearranging regions is given by

$$z^* = \frac{s_{conf}^* N_A}{S_{conf}}, \quad (6.53)$$

where $s_{conf}^* \approx k \ln 2$ is the configurational entropy of such a minimally sized region.

Substituting Equation (6.53) for z^* into Equation (6.51), the average transition probability is found to be

$$\langle p(T) \rangle = \langle A \rangle \exp \left(-\frac{s_{conf}^* N_A \delta \mu}{k T S_{conf}} \right) \quad (6.54)$$

$$= \langle A \rangle \exp \left(-\frac{C}{T S_{conf}} \right). \quad (6.55)$$

Since the molecular relaxation time τ is inversely proportional to $\langle p(T) \rangle$, we have the important conclusion that

$$\tau \propto \exp \left(\frac{C}{T S_{conf}} \right) \approx \exp \left(\frac{C}{T \Delta s} \right), \quad (6.56)$$

where Δs is the difference in entropy between the supercooled liquid and the equilibrium crystal configuration. Note that the molecular relaxation time becomes infinite in the limit of $\Delta s \rightarrow 0$.

The Adam-Gibbs model of cooperative relaxations has an important implication for Angell's classification of strong and fragile liquids.⁸⁶⁻⁸⁹ Strong liquids such as silica and germania undergo very little change in short- and intermediate-range structure as they are supercooled. This leads to a configurational entropy that is fairly independent of tempera-

ture. On the other hand, fragile liquids such as *o*-terphenyl exhibit large changes in short- and intermediate-range structure as they are supercooled. In this case, there is a strong dependence of configurational entropy on the temperature of the system. Since viscosity is directly proportional to molecular relaxation time, Equation (6.56) predicts Arrhenius behavior for strong liquids and non-Arrhenius behavior for fragile liquids, consistent with Angell’s classification criterion.

Although the Adam-Gibbs model of cooperative relaxations provides important insights into the relationship between configurational entropy and the transport coefficients of a supercooled liquid, it fails to provide a means for calculating the size of the cooperatively rearranging regions.[†] At this point, the Adam-Gibbs model provides a useful conceptual point of view.

6.5.4 Stillinger Model of Inherent Structures

The separation of configurational and vibrational contributions to the partition function, as used in the Adam-Gibbs model of cooperative relaxations,¹⁷⁰ is also a central assumption of the Stillinger model of inherent structures.^{172–177} Stillinger’s model is based on the idea presented by Goldstein¹⁷⁸ that atomic motion in a supercooled liquids consists of high-frequency vibrations in deep potential energy minima and less frequent transitions to other such minima. The transport properties of the supercooled liquid are linked to the ability of the atoms to flow among these various minima.

The Stillinger model considers a system of N particles confined to a volume V .

[†]Recently, Ngai¹⁷¹ has investigated the relationship between experimental calorimetric data and the size of the cooperatively rearranging regions in the Adam-Gibbs model. There may still be hope for calculating region size theoretically using molecular modeling and statistical mechanical techniques, assuming the regions actually exist.

The configurational coordinates of the system are denoted $\mathbf{r}_1 \cdots \mathbf{r}_N$, and the total interaction potential is given by $U(\mathbf{r}_1 \cdots \mathbf{r}_N)$. The system potential has a lower bound proportional to the number of particles, such that

$$U(\mathbf{r}_1 \cdots \mathbf{r}_N) \geq CN, \quad (6.57)$$

where C is a constant. There is no upper bound on potential owing to the high repulsive energy that exists at small separation distances. The potential energy $U(\mathbf{r}_1 \cdots \mathbf{r}_N)$ has to be continuous and at least twice differentiable with respect of the configurational coordinates $\mathbf{r}_1 \cdots \mathbf{r}_N$.

In effect, $U(\mathbf{r}_1 \cdots \mathbf{r}_N)$ represents a multidimensional energy “landscape” with many peaks and valleys. The Stillinger model divides this hypersurface into “basins,” where each basin contains a single minimum in U . This minimum represents a mechanically stable (or metastable) arrangement of the system’s particles, which is known as an “inherent structure.” The basin itself is defined to be the locus of all points in the multidimensional configuration space that “drain” to a particular minimum via steepest descent. The number Ω of basins and inherent structures in the limit of large N is given by

$$\ln \Omega \approx \ln(N! \sigma^N) + aN, \quad (6.58)$$

where σ is a symmetry factor and $a > 0$ is a constant relating to the number density N/V . The first term on the right-hand side of Equation (6.58) accounts for the symmetry of the potential energy landscape with respect to $\mathbf{r}_1 \cdots \mathbf{r}_N$, and the second term expresses the

exponential increase in the number of distinguishable inherent structures with increasing N .

The dynamics of the system moving between pairs of basins involves the transition states (first-order saddle points) between adjacent basins. There are generally on the order of N different basins adjacent to any given basin in the multidimensional configuration space; hence, there are on the order of N “exit channels” along which the system can transition between inherent structures. The underlying assumption of the Stillinger model is that while the energy landscape itself is independent of temperature, the way in which the system samples its landscape is intimately connected with the temperature of the system. Hence, the Stillinger model effectively assumes a separation of the partition function into independent configurational and vibrational components. (This assumption has been numerically validated by Sciortino, Kob, and Tartaglia¹⁷⁹ for the case of a supercooled Lennard-Jones liquid.)

The implication is that at high temperatures the system is able to freely explore the potential energy landscape since the vibrational energy generally exceeds the values for ΔU . This corresponds to the case of a liquid with high fluidity. As the liquid is supercooled, the number of available transitions decreases owing to the loss of vibrational energy. Finally, the glassy state at low temperatures corresponds to the system getting “stuck” in a single basin where ΔU is too high to overcome in laboratory time scales. Stillinger conjectures that a good glass former would have a broader distribution of basin energies than a simple liquid that easily crystallizes. With such a broader distribution, there are more opportunities to become “stuck” in a basin with an amorphous configuration.

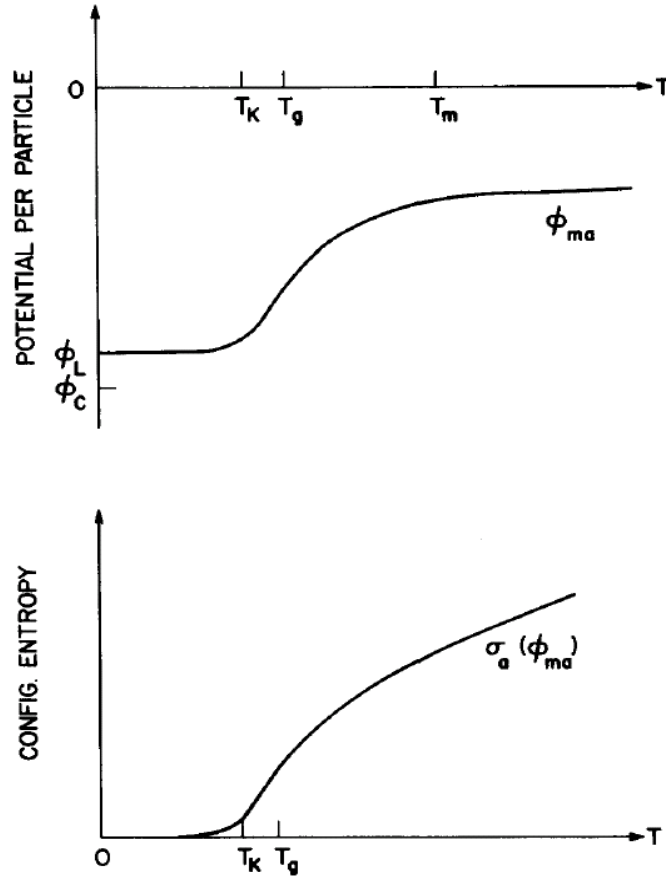


Figure 6.12. Extrapolations of potential energy and configurational entropy below the glass transition temperature, T_g , and Kauzmann temperature, T_K , according to the Stillinger model of inherent structures. Reproduced with permission from Stillinger.¹⁷⁴

(The crystalline state corresponds to the inherent structure of absolute minimum energy, $U = CN$.)

A consequence of the Stillinger model of inherent structures is that there is no strict Kauzmann temperature where the system is forced into either crystallization or an ideal glass transition. In fact, the notion of an ideal glass transition is not supported by the Stillinger model, which assumes that the glass transition is an inherently smooth process where the system configuration becomes gradually trapped in a local energy minimum.

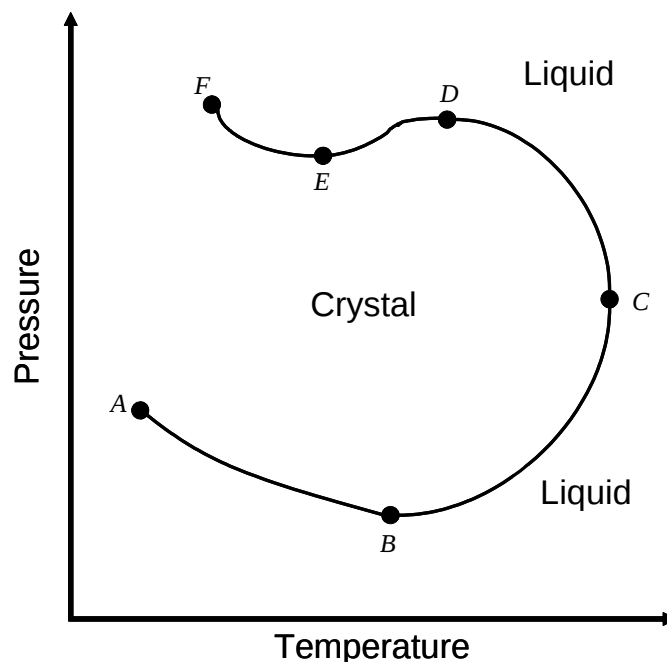


Figure 6.13. Example melting curve in the temperature-pressure plane. After Stillinger and Debenedetti.¹⁸³

Stillinger concluded that the “naive” extrapolation by Kauzmann of the thermodynamic properties of supercooled liquids to low temperatures must be incorrect. He argues that the proper extrapolations are as shown in Figure 6.12, where he shows smoothly decaying potential energy and configurational entropy curves. Since the configurational entropy of the glass reaches zero only at absolute zero, Stillinger concluded that there is no Kauzmann paradox.[‡]

While Stillinger does not agree with the existence of a Kauzmann paradox, he does concur with the notion of a Kauzmann temperature at which the entropies of two

[‡]This argument is supported by the recent experiment of Huang, Simon, and McKenna,¹⁸⁰ who measured the heat capacity of poly(α -methyl styrene) at low temperatures. They found no evidence of an ideal second-order thermodynamic transition for this system, and they hence call into question the existence of an ideal glass transition. Stillinger’s explanation is also supported by Tanaka,¹⁸¹ who uses similar reasoning as Stillinger but in terms of a glass’s resistance to crystallization at low temperatures.

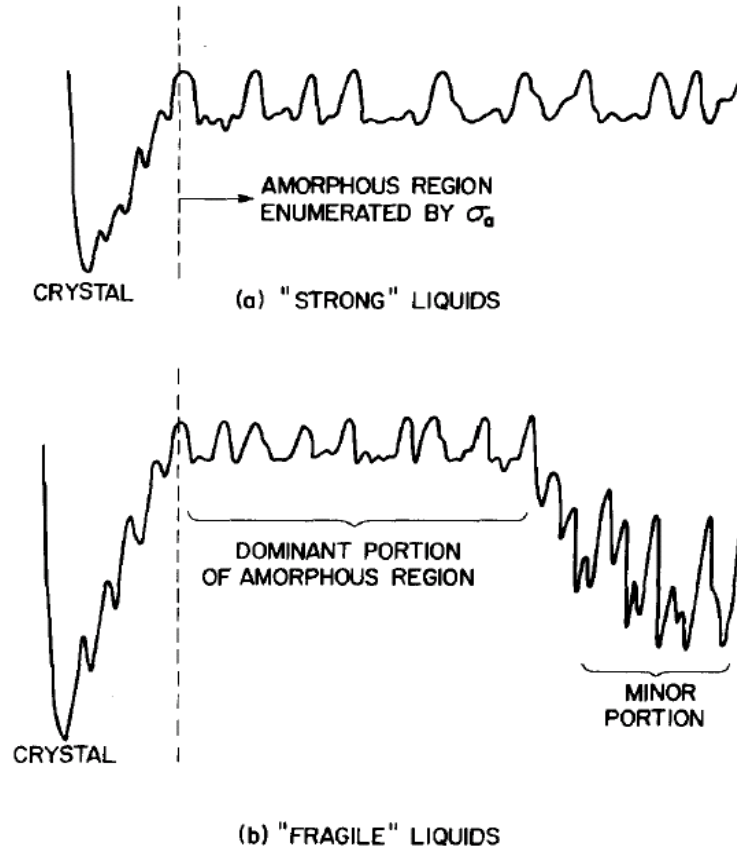


Figure 6.14. Schematic representation of the potential energy landscape for (a) “strong” and (b) “fragile” liquids. Reproduced with permission from Stillinger.¹⁷⁴

different phases of a material become equal. In fact, Stillinger extends the concept of a single Kauzmann temperature to a “Kauzmann curve” in the temperature-pressure plane of a system.^{182, 183} Consider the Claussius-Clapeyron equation that describes the slope of the melting curve in the temperature-pressure plane:

$$\frac{dp_m(T)}{dT} = \frac{S_l - S_c}{V_l - V_c}. \quad (6.59)$$

Here, $p_m(T)$ is the temperature-dependent melting pressure, and $S_{l,c}$ and $V_{l,c}$ are the molar

entropies and volumes of the liquid and crystalline phases, respectively. Figure 6.13 shows an example melting curve $ABCDEF$ to demonstrate possible melting phenomena. The “normal” melting scenario, in which the molar volume increases upon melting of a crystal, occurs between points B and C . The intervals between C and D and between E and F show the case where the molar volume decreases upon melting of a crystal, while again heat is absorbed. This corresponds to the familiar case of ice melting to form liquid water. The intervals between A and B and between D and E show the perhaps unfamiliar case of inverse melting, in which an isobaric heating of the system causes the liquid to freeze into the crystalline phase. Materials that exhibit inverse melting behavior include the helium isotopes ^3He and ^4He at low temperatures and the polymeric substance poly(4-methylpentene-1), denoted P4MP1.

Points B , D , and E in Figure 6.13 are all points of zero slope in the melting curve:

$$\frac{dp_m(T)}{dT} = 0 \quad (B, D, E). \quad (6.60)$$

Since the difference in molar volumes, $V_l - V_c$, can never be infinite, these points must have vanishing entropy change:

$$S_l - S_c = 0 \quad (B, D, E). \quad (6.61)$$

Hence, points B , D , and E are all “Kauzmann points” occurring naturally in the temperature-pressure plane, and *the existence of these Kauzmann points does not depend upon or necessitate the existence of an ideal glass transition*. Since the chemical potentials of the coexisting liquid and crystal phases are equal, the Kauzmann points must also correspond

to points of vanishing enthalpy, $\Delta H = T\Delta S$. Stillinger and Debenedetti¹⁸³ show that these Kauzmann points lie on a general “Kauzmann curve,”

$$\left(\frac{dp}{dT}\right)_{\Delta S=0} = \frac{C_{p,l} - C_{p,c}}{T(\alpha_l V_l - \alpha_c V_c)}, \quad (6.62)$$

where C_p is heat capacity and α is the isobaric thermal expansion coefficient.

The Stillinger model also has implications for Angell’s classification of strong and fragile liquids.⁸⁶ The Arrhenius behavior of the shear viscosity of strong liquids indicates that their potential energy landscape has a rather uniform roughness, as shown in Figure 6.14(a). In contrast, fragile liquids are likely to have a highly non-uniform topography in their potential energy landscape, as indicated in Figure 6.14(b). At high temperatures a fragile liquid is able to flow among basins with relatively low activation barriers, indicating the rearrangement of a small number of molecules. As the fragile liquid is supercooled, it samples deeper basins with a greater separation in the potential energy landscape. Thus, flow between these basins requires the cooperative rearrangement of many molecules and occurs less frequently than the higher temperature relaxations.

The Stillinger model of inherent structures offers important insights into the relation of the glass transition with the potential energy hypersurface of a system. However, there are computational constraints which limit this model to a theoretical study of the glass transition. The potential energy function $U(\mathbf{r}_1 \cdots \mathbf{r}_N)$ must be fully mapped out in at least a $3N$ -dimensional space in order to determine the locations and energies of the various basins, as well as the energy barriers between basins. Unfortunately, it is much too computationally demanding to fully calculate this information for a large value of N . A

hypercube modeling technique has been proposed by Kohen and Stillinger¹⁸⁴ to partially simplify the representation of U ; however, use of this technique has not been demonstrated for any system with realistic interactions or any useful value of N . In addition, the dependence of U on system volume V should be carefully considered.¹⁸⁵ Also, the Stillinger model does not specify in any detail the kinetics of flow among the various inherent structures. Stillinger's discussion of this matter is purely hypothetical, and the relationship between the potential energy hypersurface and viscous flow behavior is yet to be rigorously proven.

Further Work on Inherent Structures

Several additional researchers have studied the Stillinger model of inherent structures. Büchner and Heuer¹⁸⁶ sampled the potential energy landscape of a small system of 20 to 160 particles that interact through a model Lennard-Jones potential. They were able to determine which regions of the potential energy landscape were favorable at different temperatures, and their quantitative results support Stillinger's conjecture that deeper potential energy wells are more often sampled at lower system temperatures.

Sastry¹⁸⁷ performed a similar analysis for a binary system of 256 particles, also interacting via a model Lennard-Jones potential. Using molecular dynamics, Sastry confirmed that a faster cooling rate led the system to converge to a higher energy state than with a slower cooling rate. Sastry also found that a broader distribution of basin energies led to an increased fragility of the model liquid.¹⁸⁸ Finally, Sastry computed the configurational entropy of the binary Lennard-Jones system at low temperatures.¹⁸⁹ He found that the presence of local defects occurring in amorphous inherent structures forbids

the existence of an ideal glass transition. This result supports Stillinger’s comments on the Kauzmann paradox, at least in the framework of a binary Lennard-Jones system and Stillinger’s own model of inherent structures. Shell and coworkers¹⁹⁰ provided additional support for this finding through an analytical equation of state for a Lennard-Jones potential energy landscape, and similar computational modeling of a Lennard-Jones system was performed by Keyes.¹⁹¹

Whereas Sastry employed molecular dynamics to determine the density of states in a potential energy landscape, an alternative method using Monte Carlo sampling has been proposed by Shell, Debenedetti, and Panagiotopoulos.¹⁹² This technique is more computationally efficient than molecular dynamics, but since there is no explicit “time” variable it does not follow the true dynamics of the system. A kinetic Monte Carlo approach by Hernández-Rojas and Wales¹⁹³ incorporates time by calculating transition rates between neighboring basins. However; their approach only considers a very small sampling of the potential energy landscape and does not provide an accurate representation the different types of allowable transitions.

A random energy model by Keyes, Chowdhary, and Kim¹⁹⁴ seeks to remove some of this complexity by assuming a Gaussian distribution of basin energies. However, this is found to be a vast oversimplification, even for a Lennard-Jones model. Shell and Debenedetti¹⁹⁵ investigated the impact of changing this distribution from Gaussian to binomial. The behavior of the systems is similar in both cases, but the Gaussian distribution gave a slightly higher fragility. Similar work has been performed by Shulz.¹⁹⁶ Finally, La Nave and coworkers¹⁹⁷ have derived an expression to compute the pressure of an inherent

structure.

6.5.5 Other Thermodynamic Models

Thus far, our discussion of thermodynamic modeling of the glass transition has focused on those models which have had the greatest influence on our thinking and interpretation of the glass transition. In this section, we briefly describe several newer thermodynamic models that offer different viewpoints on the glass transition.

Kivelson and Tarjus¹⁹⁸ propose a theory of frustration-limited domains that is similar to the Adam-Gibbs and Stillinger models. According to their model, as a liquid is supercooled its constituent domains become “frustrated,” i.e., unable to relax to lower energy configurations. Complete frustration of the supercooled liquid domains leads to a transition to the glassy state.

A thermodynamic model by Speedy¹⁹⁹ assumes that the free energy of a liquid can be expressed in terms of the free energy of all the glasses that it rapidly samples. By assuming that the heat capacity of all these possible glasses is identical, Speedy’s model suggests the existence of a thermodynamic glass transition underlying the kinetics of structural relaxation. She also concludes that the fragility of a liquid is directly related to the number of unique glassy structures it can form.

Mansfield²⁰⁰ developed an empirical thermodynamic model of the glass transition that reproduces the known relaxation behavior of a supercooled liquid. However, it is not based on fundamental physics and does not add any new insights into glass transition range behavior.

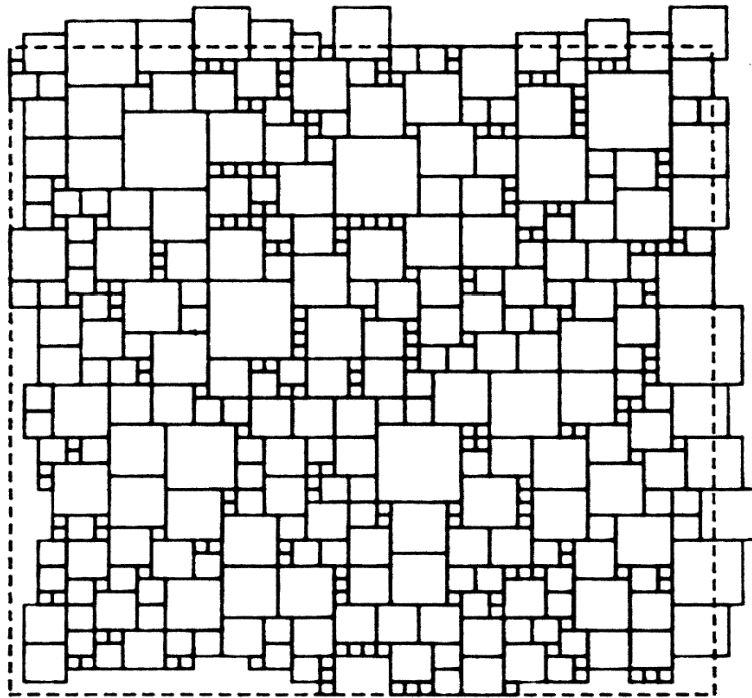


Figure 6.15. Example system configuration in the two-dimensional tiling model. Reproduced with permission from Weber, Frederickson, and Stillinger.²⁰¹

6.6 Kinetic Models

We now turn our attention to kinetic models of the glass transition, which focus on the dynamics of structural relaxation in the supercooled liquid and glass transformation ranges.

6.6.1 Tiling Model

The tiling model of Weber and Stillinger^{201,202} is based on the Adam-Gibbs concept of cooperatively rearranging regions. The tiling model considers a periodic two-dimensional system divided into square tiles of various sizes. The smallest tile has the normalized dimensions 1×1 , and larger tiles are of the size $j \times j$, where j is an integer.

An example tile configuration is shown in Figure 6.15. Each tile represents one internally homogeneous domain, and the boundaries between tiles represent locations of high energy due to strained bonds, etc.

The potential energy of the system is

$$U = 2\lambda \sum_{j \geq 1} j n_j, \quad (6.63)$$

where λ is a normalized energy and n_j is the number of $j \times j$ tiles in the system. The absence of vacancies or overlaps imposes the constraint

$$\sum_{j \geq 1} j^2 n_j = N, \quad (6.64)$$

where N is the total area of the system. The minimum energy configuration occurs when the system consists of a single tile, thereby eliminating all of the high-energy boundaries. Similarly, the maximum possible energy occurs when the system consists exclusively of 1×1 tiles. Therefore, we know that

$$2N^{-1/2} \leq \frac{U}{\lambda N} \leq 2. \quad (6.65)$$

The tiling model allows for two different types of transitions, aggregation and boundary shift, and their corresponding reverse transitions, fragmentation and coalescence. With aggregation, a square arrangement of p^2 tiles of size $q \times q$ can join together to form a single tile of size $pq \times pq$. The reverse process can occur with fragmentation, in which a large $pq \times pq$ tile is divided into p^2 tiles of size $q \times q$. A boundary shift transition occurs when a $(p+1) \times (p+1)$ tile fragments into a $p \times p$ tile and an L -shaped array of $2p+1$

unit squares. The reverse transition is coalescence.

The rate of aggregation is chosen as

$$r_a = \nu_0 \alpha^{2pq(p-1)}, \quad (6.66)$$

where ν_0 is the frequency of transition attempts and α is a rate parameter with the constraint $0 < \alpha < 1$. The reverse fragmentation rate follows from detailed balancing:

$$r_f = \nu_0 \alpha^{2pq(p-1)} \exp[-2\lambda pq(p-1)/kT]. \quad (6.67)$$

The rate of coalescence is

$$r_c = \nu_0 \alpha^{4p}, \quad (6.68)$$

and the rate of boundary shift is

$$r_b = \nu_0 \alpha^{4p} \exp(-4\lambda p/kT). \quad (6.69)$$

Clearly, it follows from Equation (6.63) that the average tile size should increase as the temperature of the system is lowered. However, the rates of aggregation and coalescence decrease with increasing tile size, and as time progresses it becomes increasingly difficult to find tiles in the proper arrangement to allow for either of these transitions. This creates a kinetic barrier in the progression toward a low-energy configuration of large tiles at low temperature, and it introduces sluggish dynamics that eventually lead to a glass transition-type behavior.

Weber and Stillinger studied the relaxation behavior of the tiling model using Monte Carlo simulations. They found that the energy autocorrelation function

$$\phi(t) = \frac{\langle U(t)U(0) \rangle - \langle U \rangle^2}{\langle U^2 \rangle - \langle U \rangle^2} \quad (6.70)$$

could be fit using a stretched exponential function of the Kohlrausch-Williams-Watts (KWW) form:

$$\phi(t) = \exp \left[- (t/\tau)^b \right], \quad (6.71)$$

where τ and b are adjustable parameters. This form of a response function can be used in the Narayanaswamy model of structural relaxation. The tiling model shows that even a highly idealized formulation can still capture some of the underlying physics of a real, complex system.

6.6.2 Mode-Coupling Theory

Mode-coupling theory refers to a set of techniques in nonequilibrium statistical mechanics used to study the anomalous properties of certain transport coefficients. For example, the viscosity of a fluid can be determined from the long time tail of a stress correlation function, where the stress tensor couples naturally with a product of two fluid velocity modes.²⁰³ Mode-coupling theory leads to a separation of time scales in which a time correlation function is divided into separate rapidly and slowly decaying portions.

As applied to supercooled liquids, mode-coupling theory is based on the following three notions:²⁰⁴

1. Shear stress relaxation occurs primarily through diffusive motion.
2. Diffusivity is inversely related to viscosity.
3. Shear viscosity is proportional to the shear stress relaxation time.

The combination of the three above relations leads to a viscosity-feedback mechanism. This may be described by first writing shear viscosity η as the product

$$\eta = G_{\infty} \tau, \quad (6.72)$$

where G_{∞} is the instantaneous elastic shear modulus and τ is the shear relaxation time. In the limit of slow structural relaxation, the shear relaxation time may be written as the sum of (fast) vibrational and (slow) structural contributions such that

$$\eta \approx G_{\infty} \tau_{vib} + G_{\infty} c(T) D^{-1} = \eta_0(T) + b(T) D^{-1}, \quad (6.73)$$

where it is assumed that the structural relaxation time is inversely related to the diffusion coefficient D , and $b(T)$ and $c(T)$ can be determined from microscopic theory. Using the Stokes-Einstein relation,

$$D = \frac{kT}{6\pi a \eta}, \quad (6.74)$$

where a is the molecular radius, we may rewrite the viscosity as

$$\eta = \eta_0(T) + \left[\frac{6\pi a b(T)}{kT} \right] \eta = \eta_0(T) + B(T) \eta. \quad (6.75)$$

Therefore, we have

$$\eta = \frac{\eta_0(T)}{1 - B(T)}. \quad (6.76)$$

In other words, the viscosity controls the shear relaxation time and hence the viscosity itself.

With mode-coupling theory, vitrification is viewed as a transition from ergodic to non-ergodic behavior[§] in terms of the relaxation behavior of the density fluctuations.^{206,207}

The van Hove density-density correlation function¹⁶⁷ is

$$\Lambda(\mathbf{r}, t) = \rho^{-1} \langle \rho(\mathbf{r}, t) \rho(\mathbf{0}, 0) \rangle \quad (6.77)$$

$$= N^{-1} \left\langle \sum_{i=1}^N \sum_{j=1}^N \int \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_i(t)] \delta[\mathbf{r}' - \mathbf{r}_j(0)] d\mathbf{r}' \right\rangle \quad (6.78)$$

$$= N^{-1} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r} + \mathbf{r}_j(0) - \mathbf{r}_i(t)] \right\rangle, \quad (6.79)$$

where ρ is the bulk number density, $\rho(\mathbf{r})$ is the number density at $\mathbf{r}$, N is the number of atoms in the system, and δ is the Dirac delta function. The Fourier transform of $\Lambda(\mathbf{r}, t)$ with respect to spatial coordinates is

$$F_{\mathbf{k}}(t) = \int \Lambda(\mathbf{r}, t) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}, \quad (6.80)$$

and the static structure factor is $S_{\mathbf{k}} = F_{\mathbf{k}}(0)$. In the ergodic (liquid) regime, $F_{\mathbf{k}}$ should decay to zero in the limit of long time. However, after vitrification the system is non-ergodic due to structural arrest; in this case the density fluctuations cannot be fully relaxed, so $F_{\mathbf{k}}$

[§]It should be noted that a prior statistical mechanical model of Jäckle²⁰⁵ also viewed the glass transition as a shift from ergodic to non-ergodic behavior, the non-ergodic glass having a finite residual entropy that is dependent on both structural and vibrational properties. In the non-ergodic glassy regime, entire regions of phase space become inaccessible due to structural arrest.¹⁶⁷

will decay to some finite value at long time. Therefore,

$$\lim_{t \rightarrow \infty} F_{\mathbf{k}}(t) = 0, \text{ liquid,} \quad (6.81)$$

$$\lim_{t \rightarrow \infty} F_{\mathbf{k}}(t) \neq 0, \text{ glass.} \quad (6.82)$$

We may write a differential equation for $F_{\mathbf{k}}(t)$ normalized to $S_{\mathbf{k}}$ as

$$\ddot{\Phi}_{\mathbf{k}}(t) + \nu_0 \dot{\Phi}_{\mathbf{k}}(t) + \Omega_{\mathbf{k}}^2 \Phi_{\mathbf{k}}(t) + \Omega_{\mathbf{k}}^2 \int_0^t \Gamma_{\mathbf{k}}(t-t') \dot{\Phi}_{\mathbf{k}}(t') dt' = 0, \quad (6.83)$$

where $\Phi_{\mathbf{k}}(t) = F_{\mathbf{k}}(t) S_{\mathbf{k}}^{-1}$, and $\Gamma_{\mathbf{k}}(t)$ is a memory function.^{207,208} The damping constant ν_0 is

$$\nu_0 = \left(\frac{kT}{m} \right)^{1/2}, \quad (6.84)$$

where m is the mass of the molecule, and the characteristic frequency $\Omega_{\mathbf{k}}$ is given by

$$\Omega_{\mathbf{k}}^2 = (\mathbf{k}\nu_0)^2 S_{\mathbf{k}}^{-1}. \quad (6.85)$$

The feedback mechanism in Equation (6.76) enters the theory through the dependence of $\Gamma_{\mathbf{k}}(t)$ on $\Phi_{\mathbf{k}}(t)$, which we may determine using Laplace transforms.²⁰⁸ Defining the Laplace transform of $\Phi_{\mathbf{k}}(t)$ as

$$\Phi_{\mathbf{k}}(z) = i \int_0^\infty \Phi_{\mathbf{k}}(t) \exp(izt) dt, \quad (6.86)$$

and accounting for the initial conditions, $\Phi_{\mathbf{k}}(0) = 1$ and $\dot{\Phi}_{\mathbf{k}}(0) = 0$, we may rewrite

Equation (6.83) as

$$\Phi_{\mathbf{k}}(z) = - \left(z - \frac{\Omega_{\mathbf{k}}^2}{z + M_{\mathbf{k}}(z)} \right)^{-1}, \quad (6.87)$$

where

$$M_{\mathbf{k}}(z) = i\nu_0 + \Omega_{\mathbf{k}}^2 \Gamma_{\mathbf{k}}(z), \quad (6.88)$$

and $\Gamma_{\mathbf{k}}(z)$ is the Laplace transform of $\Gamma_{\mathbf{k}}(t)$.

In general, the dependence of $\Gamma_{\mathbf{k}}(t)$ on $\Phi_{\mathbf{k}}(t)$ may be written in series form as

$$\Gamma_{\mathbf{k}}(t) = \sum_{m=1}^{m_0} \frac{1}{m!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_m} V^{(m)}(\mathbf{k}, \mathbf{k}_1, \dots, \mathbf{k}_m) \Phi_{\mathbf{k}_1}(t) \cdots \Phi_{\mathbf{k}_m}(t), \quad (6.89)$$

where $V^{(m)}$ is called a vertex function,¹⁶⁷ and m_0 is the number of mode-couplings. For example, the two-mode approximation of Bengtzelius, Götze, and Sjölander²⁰⁷ has

$$\Gamma_{\mathbf{k}}(t) = (2\pi)^{-3} \int V^{(2)}(\mathbf{k}, \mathbf{k}') \Phi_{\mathbf{k}'}(t) \Phi_{|\mathbf{k}-\mathbf{k}'|}(t) d\mathbf{k}'. \quad (6.90)$$

The two-mode vertex function can be determined using a kinetic theory for dense atomic liquids:

$$V^{(2)}(\mathbf{k}, \mathbf{k}') = \left(\frac{\rho k T}{m} \right) (\hat{\mathbf{k}} \cdot \mathbf{k}) c(\mathbf{k}') S(\mathbf{k}') S(|\mathbf{k} - \mathbf{k}'|) \quad (6.91)$$

$$\times \left\{ (\hat{\mathbf{k}} \cdot \mathbf{k}) c(\mathbf{k}') + [\hat{\mathbf{k}} \cdot (\mathbf{k} - \mathbf{k}')] c(|\mathbf{k} - \mathbf{k}'|) \right\}, \quad (6.92)$$

where $\hat{\mathbf{k}} = \mathbf{k} |\mathbf{k}|^{-1}$ and $c(\mathbf{k})$ is the Fourier transform of the direct correlation function,

$$\rho c(\mathbf{k}) = \frac{S(\mathbf{k}) - 1}{S(\mathbf{k})}. \quad (6.93)$$

The static structure factor can be calculated by¹⁶⁷

$$S(\mathbf{k}) = 1 + 4\pi\rho \int r^2 g(r) (kr)^{-1} \sin(kr) dr \quad (6.94)$$

where $g(r)$ is the pair distribution function⁶⁶ and can be obtained from knowledge of the molecular interaction potentials.

Hence, we have outlined a (two-)mode-coupling model of the kinetics of supercooled liquids in which the only input is the static structure factor at a given density and temperature. Rewriting the vitrification condition in the Laplace domain,²⁰⁸ we have

$$\lim_{z \rightarrow 0} \Phi_{\mathbf{k}}(z) = -\frac{f_{\mathbf{k}}}{z}, \quad (6.95)$$

where $f_{\mathbf{k}}$ is the non-ergodicity parameter. Combining this with Equations (6.87) and (6.88), we may obtain the long time limit of the memory function:

$$\Gamma_{\mathbf{k}}(t \rightarrow \infty) = \frac{f_{\mathbf{k}}}{1 - f_{\mathbf{k}}}. \quad (6.96)$$

Glassy states correspond to those temperature and density conditions that lead to nonzero solutions for $f_{\mathbf{k}}$; zero solutions for $f_{\mathbf{k}}$ pertain to the supercooled liquid.¹⁶⁷

Therefore, mode-coupling theory yields a locus of points in the (ρ, T) plane that

correspond to sharp transitions from ergodic to non-ergodic behavior, which is associated with an ideal glass transition.²⁰⁹ The problems with this approach are obvious: a sudden structural arrest is not physical, and the concept of an ideal glass transition does not correspond to what is observed in experiment. Furthermore, vitrification does not necessitate that the system should become non-ergodic. Subsequent extensions to mode-coupling theory^{210–212} incorporating coupling between density and momentum fluctuations have restored the ergodicity of the system at low temperatures via activated diffusion. This newer version of the theory leads to a smooth glass transition; however, there is often large disagreement among particular implementations of mode-coupling theory,²¹³ and there exist large discrepancies between the glass transition range behavior predicted by mode-coupling theory and that observed in experiment.¹⁶⁷

Whereas mode-coupling theory has been hitherto unsuccessful at predicting glass transition range behavior (its original intent), it has shown remarkable success at describing relaxations in supercooled liquids above the glass transition temperature.^{214–217} Mode-coupling theory is able to make detailed prediction about relaxation dynamics on an intermediate time scale between the microscopic and hydrodynamic limits. In particular, mode-coupling theory has successfully reproduced the non-Arrhenius behavior of viscosity and diffusivity in a supercooled Lennard-Jones system.²¹⁴ However, the mode-coupling approach has the apparently unrealistic feature that the relaxation returns to exponential behavior in the limit of long time; there is no experimental evidence to support this theoretical prediction.¹⁶⁷

Finally, we note that the two-step relaxation process in mode-coupling theory is

often confused with the so-called α and β processes of supercooled and glassy dynamics.¹⁶⁷ The term “ α relaxation” refers to cooperative relaxation of molecules that occurs on the order of 1-10 seconds; “ β relaxation” refers to the faster, non-collective motion that occurs on the order of 10^{-5} seconds. Whereas the β relaxation curve is always Arrhenius, the α relaxation curve becomes increasingly non-Arrhenius as the system is cooled toward the glass transition temperature. In the framework of Stillinger’s model of inherent structures,¹⁷⁴ α relaxation involves the sampling of deep, separated potential energy minima; β relaxation involves the sampling of contiguous minima with low transition energy. After vitrification, α motion becomes suppressed but β motion still persists. As a glass is heated, the α process becomes re-activated as cooperative molecular motions are once again possible. At high temperatures the α and β processes become indistinguishable since all inherent structures are readily accessible. Since mode-coupling theory also involves separate slow and fast relaxation processes, it is common to label these two processes as “ α ” and “ β ” motions. However, this notion is incorrect and confusing because in the high temperature regime where mode-coupling theory is most applicable there is no distinction between exploration of deep potential energy minima and the noncollective exploration of local minima.¹⁶⁷

6.6.3 Molecular Dynamics

With molecular dynamics, each atom or molecule in a system is represented as a point particle with a position and velocity. The interactions between particles are described by a set of force fields that are determined by quantum mechanical calculations or with empirical fitting. The system propagates forward in time by numerically integrating Newton’s equations of motion. Unfortunately, accurate implementation of molecular dynamics re-

quires time steps on the order of 10^{-15} seconds. If we consider a system of several thousand particles, it is difficult to simulate times much longer than 10^{-7} - 10^{-6} seconds.²¹⁸ Since the α process involves relaxations on the order of 1-10 seconds, it is computationally infeasible to simulate realistic glass transition behavior using molecular dynamics. Most attempts at simulating the glass transition with molecular dynamics involve highly unrealistic quenching schemes^{219,220} and should be treated with great caution.

6.7 Conclusions

We have reviewed several phenomenological, thermodynamic, and kinetic models of the glass transition. While none of these models offers a complete description of glass transition range behavior, we may draw important conclusions from each:

- The Tool concept of a single fictive temperature¹⁵³ is useful in contemplating the nonequilibrium nature of glass, although Ritland¹⁵⁴ has shown this picture to be inadequate.
- The Narayanaswamy model of relaxation¹⁵⁷ includes the possibility of multiple relaxation modes occurring on different time scales, thereby incorporating complex thermal history.
- The free volume model^{164,165} is based on a direct correlation between the fluidity of a supercooled liquid and its free volume; however, this type of correlation is inadequate and may need rethinking.¹⁶⁶
- The Gibbs-DiMarzio model¹⁶⁹ shows the type of conditions that would be necessary

to achieve an ideal glass transition.

- The Adam-Gibbs model¹⁷⁰ is based on the compelling notion of cooperative relaxations, but it does not address the issue of how to calculate the size of the cooperatively rearranging regions.
- The Stillinger model of inherent structures¹⁷⁴ relates structural relaxation to the sampling of a potential energy landscape which is independent of temperature. This is the most firmly grounded model discussed in this chapter; however, Stillinger addresses neither the computation of this potential energy landscape nor the details of kinetic modeling based on this approach.
- The highly idealized, two-dimensional tiling model^{201,202} shows kinetics similar to that of a real glass-forming liquid.
- Mode-coupling theory^{204–208} is based on a viscosity-feedback mechanism and the separation of fast and slow time scales. While it has not been successful at predicting glass transition range behavior, it has been useful in describing relaxations in supercooled liquids above the glass transition temperature.^{214–217}

Chapter 7

Nonequilibrium Statistical Mechanical Model of the Glass Transition

As we have seen, previous models of the glass transition include the phenomenological models of Tool¹⁵³ and Narayanaswamy,¹⁵⁷ which rely on experimental fitting parameters and can thus provide for only *a posteriori* calculations of transition range behavior. The free volume model^{164,165} is based on a direct correlation between the fluidity of a supercooled liquid and its free volume; however, this type of correlation has been shown to be inadequate.¹⁶⁶ The thermodynamic models of Gibbs-DiMario¹⁶⁹ and Adam-Gibbs¹⁷⁰ give important insights into the nature of the glass transition, but the inherent assumptions in these models unfortunately restrict their utility to real systems. Kinetic models such as mode-coupling theory^{206,207} show promise, but they have not been able to successfully

reproduce glass transition range behavior.¹⁶⁷

In this chapter, we propose a new model of structural relaxation in glass based on nonequilibrium statistical mechanics²⁰³ and the Stillinger concept of inherent structures.^{172–177} Using this model, we demonstrate for the first time numerically the connection between potential energy landscape and the fragility of a supercooled liquid.

7.1 Model Derivation

Consider a system of N atoms or molecules with coordinates $\mathbf{r}_1 \cdots \mathbf{r}_N$. Based on the Stillinger model of inherent structures,^{172–177} the total interaction potential of the system is a function of its coordinates,

$$U(\mathbf{r}_1 \cdots \mathbf{r}_N) \geq CN, \quad (7.1)$$

where C is a constant. The lower bound on potential energy corresponds to the minimum energy configuration of a crystalline structure; there is no upper bound owing to the high repulsive energy that exists at small separation distances. The potential energy $U(\mathbf{r}_1 \cdots \mathbf{r}_N)$ is continuous and at least twice differentiable with respect of the configurational coordinates $\mathbf{r}_1 \cdots \mathbf{r}_N$.

In effect, $U(\mathbf{r}_1 \cdots \mathbf{r}_N)$ represents a $3N$ -dimensional energy landscape with many peaks and valleys. The Stillinger model divides this hypersurface into basins, where each basin contains a single minimum in U . This minimum represents a mechanically stable (or metastable) arrangement of the system’s particles, which is known as an “inherent structure.” The basin itself is defined to be the locus of all points in the multidimensional

configuration space that “drain” to a particular minimum via steepest descent. The number Ω of basins and inherent structures in the limit of large N is given by

$$\ln \Omega \approx \ln (N!s^N) + aN, \quad (7.2)$$

where s is a symmetry factor and $a > 0$ is a constant relating to the number density N/V . The first term on the right-hand side of Equation (7.2) accounts for the symmetry of the potential energy landscape with respect to $\mathbf{r}_1 \cdots \mathbf{r}_N$, and the second term expresses the exponential increase in the number of distinguishable inherent structures with increasing N .

The dynamics of the system moving between pairs of basins involves the transition states (first-order saddle points) between adjacent basins. The underlying assumption of the Stillinger model is that while the potential energy landscape itself is independent of temperature, the way in which the system samples this landscape depends directly on its kinetic energy, and thus the temperature of the system. At high temperatures, the system has ample kinetic energy to flow freely between basins; this corresponds to the case of a liquid with high fluidity. As the liquid is supercooled, the number of available basin transitions decreases owing to the loss of kinetic energy. Finally, the glassy state at low temperatures corresponds to the system getting “stuck” in a single basin where the potential energy barrier for a transition is too high to overcome in laboratory time scales. In this way, the Stillinger model effectively assumes a separation of the partition function into independent configurational and vibrational components.

Based on the above Stillinger model, we may construct an $\Omega \times \Omega$ potential energy

matrix,

$$\mathbf{U} = \begin{pmatrix} U_{11} & U_{12} & U_{13} & \cdots & U_{1\Omega} \\ U_{21} & U_{22} & U_{23} & \cdots & U_{2\Omega} \\ U_{31} & U_{32} & U_{33} & \cdots & U_{3\Omega} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ U_{\Omega 1} & U_{\Omega 2} & U_{\Omega 3} & \cdots & U_{\Omega \Omega} \end{pmatrix}, \quad (7.3)$$

where the diagonal elements ($U_{\alpha\alpha}$) are the inherent structure energies and the off-diagonal elements ($U_{\alpha\beta}$, $\alpha \neq \beta$) are the transition energies from basin α to basin β . The matrix $\mathbf{U}$ is symmetric by construction ($U_{\alpha\beta} = U_{\beta\alpha}$). In order to capture all “memory” effects that can occur in a glassy system, we have the initial condition of an equilibrium liquid at the melting temperature T_m . From equilibrium statistical mechanics, the initial phase space distribution for any basin α is

$$f_{\alpha}^{eq} = \frac{1}{Q} \exp\left(-\frac{U_{\alpha\alpha}}{kT_m}\right), \quad (7.4)$$

where k is Boltzmann’s constant and Q is the partition function

$$Q = \sum_{\alpha=1}^{\Omega} \exp\left(-\frac{U_{\alpha\alpha}}{kT_m}\right). \quad (7.5)$$

In addition, we know that

$$\sum_{\alpha=1}^{\Omega} f_{\alpha}^{eq} = 1. \quad (7.6)$$

Rewriting the above three expressions in matrix notation, we have

$$\mathbf{f}^{eq} = \frac{1}{Q} \exp \left(-\frac{\hat{P}\mathbf{U}}{kT_m} \right); \quad (7.7)$$

$$Q = \text{Trace} \left\{ \exp \left(-\frac{\hat{P}\mathbf{U}}{kT_m} \right) \right\}; \quad (7.8)$$

$$\text{Trace} \{f^{eq}\} = 1; \quad (7.9)$$

where $\hat{P}$ is the tetradic projection operator defined by

$$\hat{P}_{jk,lm} = \delta_{jk}\delta_{jl}\delta_{km} \quad (7.10)$$

such that

$$\left(\hat{P}\mathbf{U} \right)_{jk} = \sum_{l,m} P_{jk,lm} U_{lm} = \delta_{jk} U_{jj}. \quad (7.11)$$

In other words, $\hat{P}\mathbf{U}$ returns a new matrix containing just the diagonal elements of $\mathbf{U}$; since $\hat{P}$ is a projection operator, $\hat{P}\hat{P}\mathbf{U} = \hat{P}\mathbf{U}$.

As we cool the equilibrium liquid into the supercooled liquid and glassy regimes, the relaxation time (i.e., the time it takes to reach equilibrium) exceeds the experimental measurement time. We are interested in calculating the phase space distribution of the system as it relaxes, which may be accomplished using nonequilibrium statistical mechanical techniques.

Since the phase space distribution function is a conserved quantity, i.e.,

$$\text{Trace} \{ \mathbf{f}(t) \} = 1 \quad (7.12)$$

for all time t , its evolution in time is governed by the Liouville equation,

$$\frac{\partial}{\partial t} \mathbf{f}(t) = -\hat{L} \mathbf{f}(t); \quad \mathbf{f}(0) = \mathbf{f}_{eq}, \quad (7.13)$$

where $\hat{L}$ is the Liouville operator defined in terms of a Poisson bracket with the system Hamiltonian:

$$\hat{L} = [H,]_{P.B.} = \frac{\partial H}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{q}} - \frac{\partial H}{\partial \mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{p}}. \quad (7.14)$$

Equation (7.13) has the exact solution

$$\mathbf{f}(t) = e^{-t\hat{L}} \mathbf{f}^{eq}, \quad (7.15)$$

where $e^{-t\hat{L}}$ is a new operator that propagates the phase space distribution forward in time.

Ultimately, what we care about is not $\mathbf{f}(t)$ but the evolution of some experimentally measurable property A used to monitor the relaxation process, such as volume, heat capacity, or any other thermophysical property of interest. The phase space average of A at any time t is simply

$$\langle A(t) \rangle = \text{Trace} \{ \mathbf{f}(t) \cdot \mathbf{A} \} = \text{Trace} \left\{ e^{-t\hat{L}} \mathbf{f}^{eq} \cdot \mathbf{A} \right\}. \quad (7.16)$$

This is the ‘‘Schrödinger’’ picture in which the time dependence is accounted for in the phase space distribution function. Taking the adjoint gives us the equivalent ‘‘Heisenberg’’ picture:

$$\langle A(t) \rangle = \text{Trace} \left\{ \mathbf{f}^{eq} \cdot e^{t\hat{L}} \mathbf{A} \right\} = \text{Trace} \{ \mathbf{f} \cdot \mathbf{A}(t) \}. \quad (7.17)$$

We have thus derived an exact solution for the general problem of glass transition range behavior. However, this depends on having full knowledge of the system Hamiltonian in order to evaluate the Poisson bracket in Equation (7.14), which may be computationally infeasible. The kinetics may be simplified by writing a master equation for each basin,

$$\frac{d}{dt}f_{\alpha}(t) = \sum_{\beta \neq \alpha}^{\Omega} K_{\beta\alpha}[T(t)] f_{\beta}(t) - \sum_{\beta \neq \alpha}^{\Omega} K_{\alpha\beta}[T(t)] f_{\alpha}(t), \quad (7.18)$$

which preserves the detailed balance condition of Equation (7.12). The rate parameters $K_{\alpha\beta,\beta\alpha}$ are defined parametrically in terms of an arbitrary cooling path, $T(t)$, and form a matrix:

$$\mathbf{K} = \begin{pmatrix} 0 & K_{12} & K_{13} & \cdots & K_{1\Omega} \\ K_{21} & 0 & K_{23} & \cdots & K_{2\Omega} \\ K_{31} & K_{32} & 0 & \cdots & K_{3\Omega} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ K_{\Omega 1} & K_{\Omega 2} & K_{\Omega 3} & \cdots & 0 \end{pmatrix}. \quad (7.19)$$

Unlike $\mathbf{U}$, $\mathbf{K}$ is not a symmetric matrix ($K_{\alpha\beta} \neq K_{\beta\alpha}$).

The master equations have been defined without any reference to the underlying kinetic model. If we assume the system is always in a state of local equilibrium, i.e., the system can always be described in terms of an inherent structure of Φ , the rate of transition from basin α to basin β is approximately

$$K_{\alpha\beta}[T(t)] \approx \frac{\omega_{\alpha}}{2\pi} \exp \left[-\frac{(U_{\alpha\beta} - U_{\alpha\alpha})}{kT(t)} \right], \quad (7.20)$$

where ω_α is the frequency factor according to transition state theory (TST). Of course, a more accurate model of $K_{\alpha\beta}$ may be substituted for Equation (7.20) without changing the underlying formulation of Equation (7.18).

7.2 Master Equation Dynamics

The set of Ω master equations can be solved by defining a transition matrix $\mathbf{W}$ with elements

$$W_{\beta\alpha} = K_{\beta\alpha} - \delta_{\beta\alpha} \sum_{\gamma \neq \alpha}^{\Omega} K_{\alpha\gamma}. \quad (7.21)$$

With this definition, Equation (7.18) can be rewritten in matrix notation as

$$\frac{d}{dt} \mathbf{f}(t) = \mathbf{W}[T(t)] \mathbf{f}(t). \quad (7.22)$$

This can be solved by discretizing the temperature function $T(t)$ into a stepwise function where $T(t) = T$ is constant within each step. Within each temperature step $\mathbf{W}$ is independent of time, so we can write

$$\frac{d}{dt} \mathbf{f}(t) = \mathbf{W} \mathbf{f}(t). \quad (7.23)$$

Following a similar approach as Wales,²²⁵ the solution to Equation (7.23) can be found by exploiting the detailed balance condition

$$K_{\alpha\beta} f_\alpha^{eq} = K_{\beta\alpha} f_\beta^{eq}, \quad (7.24)$$

where f_α^{eq} and f_β^{eq} denote equilibrium values of f_α and f_β at the current temperature. This detailed balance condition can be used to construct a new symmetric transition matrix $\tilde{\mathbf{W}}$ according to

$$\tilde{W}_{\beta\alpha} = \sqrt{\frac{f_\beta^{eq}}{f_\alpha^{eq}}} W_{\beta\alpha} = \sqrt{\frac{f_\beta^{eq}}{f_\alpha^{eq}}} \left(K_{\beta\alpha} - \delta_{\beta\alpha} \sum_{\gamma \neq \alpha}^{\Omega} K_{\alpha\gamma} \right). \quad (7.25)$$

From Equation (7.24) we know that

$$\sqrt{\frac{f_\beta^{eq}}{f_\alpha^{eq}}} = \sqrt{\frac{K_{\alpha\beta}}{K_{\beta\alpha}}}. \quad (7.26)$$

The elements of $\tilde{\mathbf{W}}$ simplify to

$$\tilde{W}_{\beta\alpha} = \sqrt{\frac{K_{\alpha\beta}}{K_{\beta\alpha}}} \left(K_{\beta\alpha} - \delta_{\beta\alpha} \sum_{\gamma \neq \alpha}^{\Omega} K_{\alpha\gamma} \right), \quad (7.27)$$

or

$$\tilde{W}_{\beta\alpha} = \begin{cases} \sqrt{K_{\alpha\beta} K_{\beta\alpha}}, & \alpha \neq \beta \\ -\sum_{\gamma \neq \alpha}^{\Omega} K_{\alpha\gamma}, & \alpha = \beta \end{cases}. \quad (7.28)$$

Thus, $\tilde{\mathbf{W}}$ is manifestly symmetric, and defining

$$\tilde{f}_\alpha = \frac{f_\alpha}{\sqrt{f_\alpha^{eq}}}, \quad (7.29)$$

we can rewrite Equation (7.23) as

$$\frac{d}{dt} \tilde{\mathbf{f}}(t) = \tilde{\mathbf{W}} \tilde{\mathbf{f}}(t). \quad (7.30)$$

We can diagonalize $\tilde{\mathbf{W}}$ using a similarity transformation,

$$\mathbf{u}^{-1}\tilde{\mathbf{W}}\mathbf{u} = \boldsymbol{\lambda} = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \lambda_\Omega \end{pmatrix}. \quad (7.31)$$

Thus, we can rewrite Equation (7.30) as

$$\mathbf{u}^{-1} \frac{d}{dt} \tilde{\mathbf{f}}(t) = \mathbf{u}^{-1} \tilde{\mathbf{W}} \mathbf{u} \mathbf{u}^{-1} \tilde{\mathbf{f}}(t). \quad (7.32)$$

The unitary matrix $\mathbf{u}$ is defined by

$$\mathbf{u} = \begin{pmatrix} V_1^{(1)} & V_1^{(2)} & \cdots & V_1^{(\Omega)} \\ V_2^{(1)} & V_2^{(2)} & \cdots & V_2^{(\Omega)} \\ \vdots & \vdots & \ddots & \vdots \\ V_\Omega^{(1)} & V_\Omega^{(2)} & \cdots & V_\Omega^{(\Omega)} \end{pmatrix} = \begin{pmatrix} \mathbf{V}^{(1)} & \mathbf{V}^{(2)} & \cdots & \mathbf{V}^{(\Omega)} \end{pmatrix}, \quad (7.33)$$

where $\mathbf{V}^{(\alpha)}$ is an eigenvector of $\tilde{\mathbf{W}}$ satisfying

$$\tilde{\mathbf{W}}\mathbf{V}^{(\alpha)} = \lambda_\alpha \mathbf{V}^{(\alpha)}. \quad (7.34)$$

Defining

$$\mathbf{F}(t) = \mathbf{u}^{-1} \tilde{\mathbf{f}}(t), \quad (7.35)$$

Equation (7.32) reduces to

$$\frac{d}{dt} \mathbf{F}(t) = \boldsymbol{\lambda} \mathbf{F}(t). \quad (7.36)$$

This has the solution

$$F_\alpha(\Delta t) = F_\alpha^0 e^{\lambda_\alpha \Delta t}, \quad (7.37)$$

where F_α^0 is the value of F_α at the beginning of the temperature step and the temperature step has a duration of Δt . Transforming back to the $\tilde{f}_\alpha$ variables,

$$\tilde{f}_\alpha(\Delta t) = \sum_{\beta=1}^{\Omega} u_{\alpha\beta} F_\beta^0 e^{\lambda_\beta \Delta t}. \quad (7.38)$$

From Equation (7.29), we have

$$f_\alpha(\Delta t) = \sqrt{f_\alpha^{eq}} \sum_{\beta=1}^{\Omega} u_{\alpha\beta} F_\beta^0 e^{\lambda_\beta \Delta t}. \quad (7.39)$$

The quantity F_β^0 can be found by

$$F_\beta^0 = \sum_{\gamma=1}^{\Omega} u_{\beta\gamma}^{-1} \tilde{f}_\gamma = \sum_{\gamma=1}^{\Omega} u_{\beta\gamma}^{-1} \frac{f_\gamma}{\sqrt{f_\gamma^{eq}}}. \quad (7.40)$$

Since $\mathbf{u}$ is a unitary matrix, $u_{\beta\gamma}^{-1} = u_{\gamma\beta}$, and

$$F_\beta^0 = \sum_{\gamma=1}^{\Omega} u_{\gamma\beta} \frac{f_\gamma}{\sqrt{f_\gamma^{eq}}}. \quad (7.41)$$

Therefore,

$$f_\alpha(\Delta t) = \sqrt{f_\alpha^{eq}} \sum_{\beta=1}^{\Omega} u_{\alpha\beta} e^{\lambda_\beta \Delta t} \sum_{\gamma=1}^{\Omega} u_{\gamma\beta} \frac{f_\gamma}{\sqrt{f_\gamma^{eq}}}. \quad (7.42)$$

Using the detailed balance relation of Equation (7.26), we have the solution

$$f_{\alpha}(\Delta t) = \sum_{\beta=1}^{\Omega} u_{\alpha\beta} e^{\lambda_{\beta}\Delta t} \sum_{\gamma=1}^{\Omega} \sqrt{\frac{K_{\gamma\alpha}}{K_{\alpha\gamma}}} u_{\gamma\beta} f_{\gamma}. \quad (7.43)$$

Please note that this solution is for a single temperature step with a duration of Δt . Equation (7.43) should be applied iteratively for all temperature steps in order to calculate the full time evolution of the phase space distribution $\mathbf{f}$.

7.3 Dependence of Fragility on Potential Energy Landscape

According to Angell’s criterion,^{86–89} glass-forming liquids may be classified as either “strong” or “fragile” depending on their observed dependence of viscosity η on temperature. Strong liquids exhibit a behavior that is close to the Arrhenius form,

$$\eta = \eta_0 \exp\left(\frac{\Delta H}{kT}\right), \quad (7.44)$$

where ΔH is an activation barrier to flow and η_0 is a constant. When the logarithm of viscosity is plotted as a function of inverse temperature,⁸⁶ strong liquids will show a near-straight-line relationship. Examples of strong liquids include silica (SiO_2) and germania (GeO_2). Fragile liquids, on the other hand, exhibit a large departure from this straight-line relationship. Examples of fragile liquids include *o*-terphenyl, heavy metal halides, and calcium aluminosilicates.

Experiments have shown strong evidence for a correlation between the fragility of a supercooled liquid and the degree to which its relaxation kinetics depart from a simple

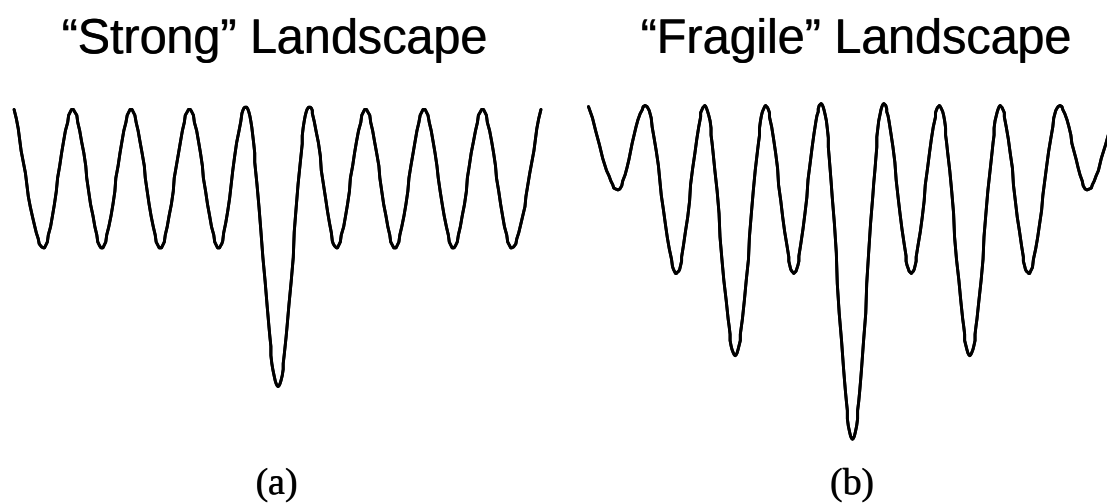


Figure 7.1. Model one-dimensional (a) “strong” and (b) “fragile” potential energy landscapes.

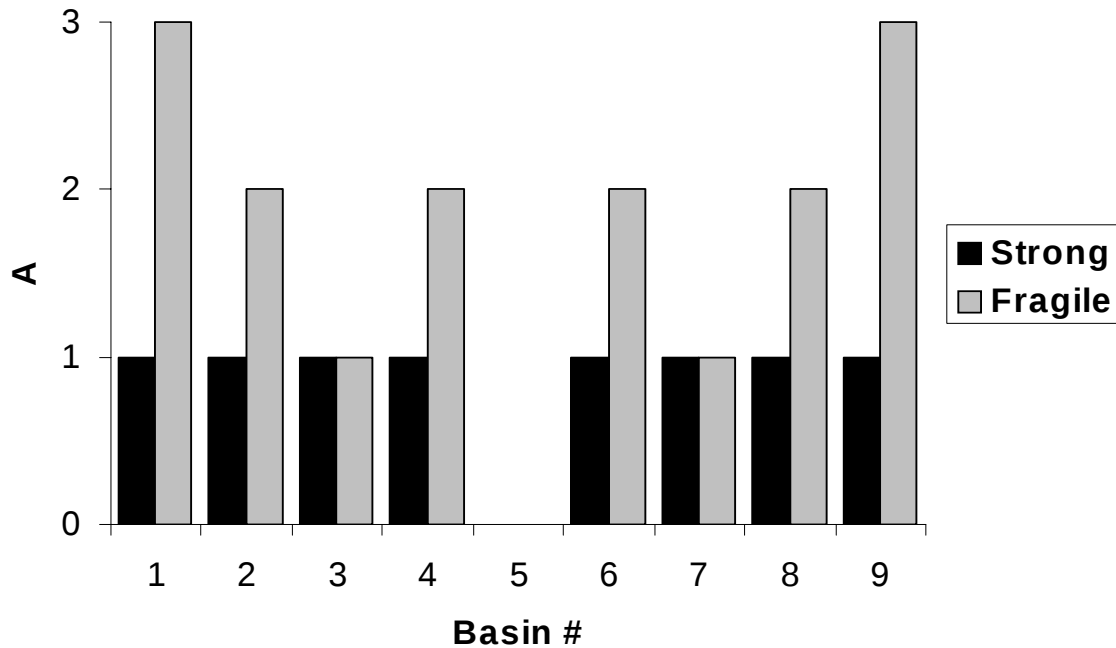


Figure 7.2. Values of the arbitrary property A for each of the nine basins in the “strong” and “fragile” landscapes of Figure 7.1.

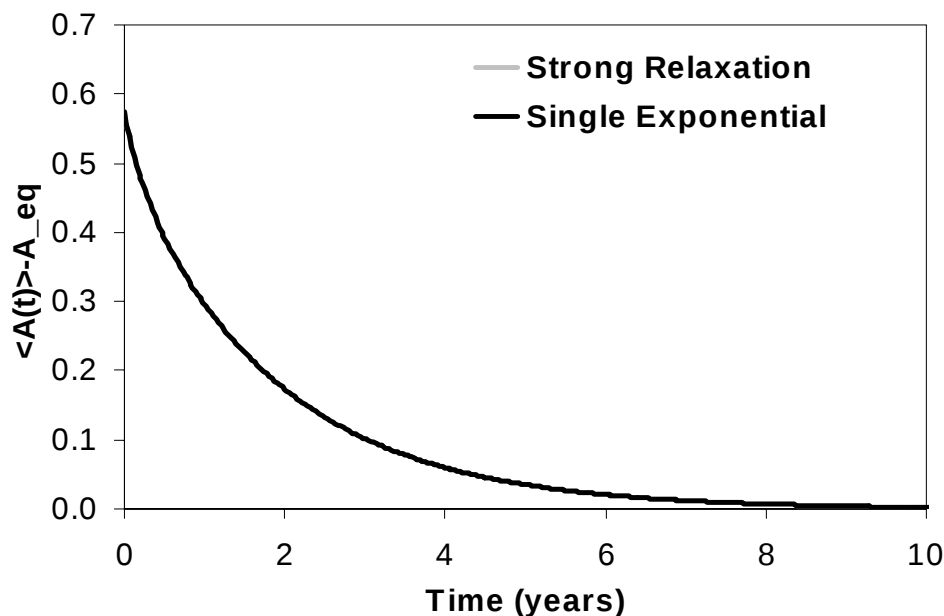


Figure 7.3. Calculated relaxation behavior of the “strong” energy landscape in Figure 7.1(a). The relaxation curve fits almost perfectly to a single exponential.

exponential decay.²²¹ Strong liquids, i.e., those exhibiting the Arrhenius viscosity behavior of Equation (7.44), also exhibit near-exponential relaxation kinetics. Fragile liquids generally show a large departure from both of these behaviors, i.e., fragile liquids have a distribution of relaxation times with different weights for each relaxation mode.

Stillinger¹⁷⁴ and Angell⁸⁸ have proposed a connection between the fragility of a glass-forming liquid and the topography of its potential energy landscape. Based on the properties of strong and fragile liquids, they have conjectured that a strong liquid should have a rather uniform topography throughout the available phase space. In contrast, fragile liquids are likely to have a highly non-uniform topography. At high temperatures a fragile liquid is able to flow among basins with relatively low activation barriers, indicating the rearrangement of a small number of molecules. As the fragile liquid is supercooled, it

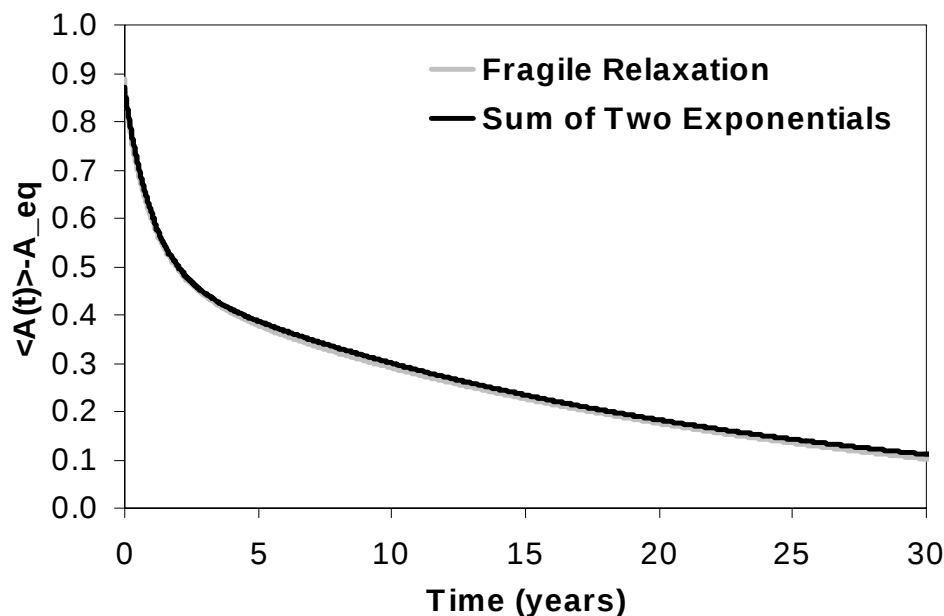


Figure 7.4. Calculated relaxation behavior of the “fragile” energy landscape in Figure 7.1(b). The relaxation curve fits very well to a sum of two exponentials.

samples deeper basins with a greater separation in the potential energy landscape. Thus, flow between these basins requires the cooperative rearrangement of many molecules and occurs less frequently than the higher temperature relaxations. While very insightful, this proposal of Stillinger and Angell has not hitherto been proven theoretically or demonstrated numerically.

Using the nonequilibrium statistical mechanical model derived in Section 7.1, we demonstrate for the first time numerically this connection between the topography of a potential energy landscape and the fragility of the system. We consider the idealized one-dimensional landscapes shown in Figure 7.1. Figure 7.1(a) shows the energy landscape of the “strong” system, which has a mostly uniform distribution of inherent structure and transition energies. A single deeper minimum is chosen so that the system will undergo

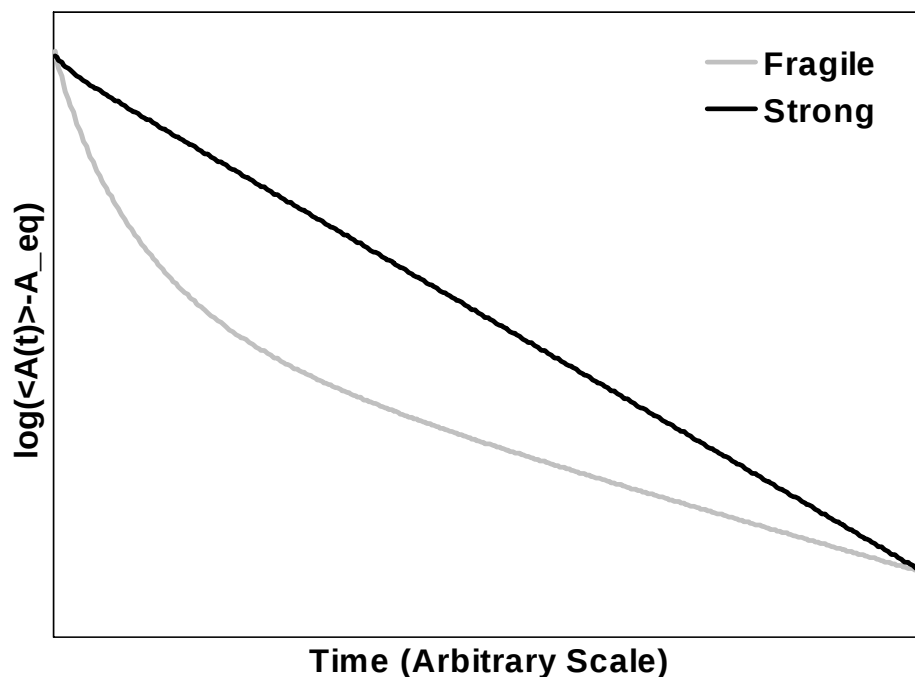


Figure 7.5. Qualitative relaxation behavior of “strong” vs. “fragile” energy landscapes in the supercooled regime. Units are arbitrary.

relaxation when changing temperature. The “fragile” landscape, shown in Figure 7.1(b), contains a wider distribution of inherent structure energies. Both the strong and fragile landscapes have nine basins and assume periodic boundary conditions.* In order to isolate the impact of inherent structure energies, all of the transition energies are chosen to be equal. Using these idealized one-dimensional systems, we compute the evolution of an arbitrary property A in time. Each basin has a particular value of A associated with it; as shown in Figure 7.2, we assume A to be proportional to the depth of the basin itself.

Figures 7.3 and 7.4 plot the ensemble average of A as a function of time, $\langle A(t) \rangle$,

*The particular basin and transition energies have been chosen arbitrarily and do not affect the qualitative differences between “strong” and “fragile” systems. In the case shown here, the difference in basin energies is on the order of 0.1 eV, and the transition energies are on the order of 1 eV. Using a frequency factor of 10 GHz, relaxation occurs over a time scale of many years.

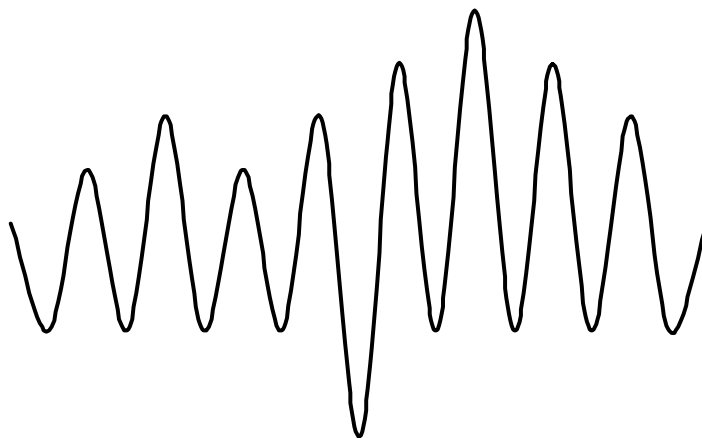


Figure 7.6. The “strong” landscape from Figure 7.1(a), with uneven transition energies.

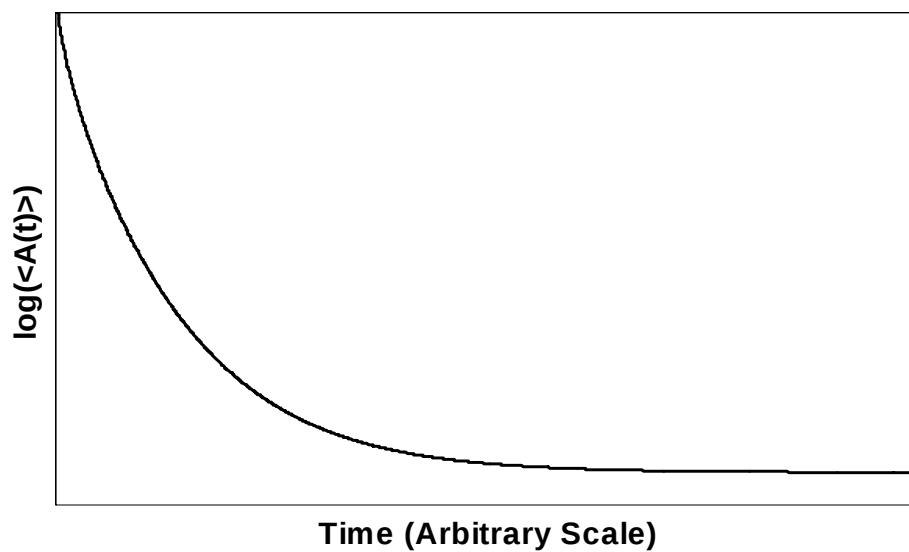


Figure 7.7. Qualitative relaxation behavior of the potential energy landscape in Figure 7.6.

assuming the systems are quenched from a high equilibrium temperature (1000 K) to room temperature and are allowed to relax in the limit of long time. Figure 7.3 shows that relaxation of the “strong” landscape of Figure 7.1(a) fits almost perfectly to a single exponential function:

$$\langle A(t) \rangle_{strong} - A_{eq_strong} = 0.5317 \exp \left(-\frac{t_{years}}{1.785} \right), \quad (7.45)$$

where A_{eq_strong} is the equilibrium value of A for the strong system at room temperature and t_{years} is time in years. In contrast, the fragile relaxation shown in Figure 7.4 exhibits a significant departure from this type of simple exponential decay. The fragile curve fits well to a sum of two exponentials:

$$\langle A(t) \rangle_{fragile} - A_{eq_fragile} = 0.3799 \exp \left(-\frac{t_{years}}{1.026} \right) + 0.4924 \exp \left(-\frac{t_{years}}{20.17} \right). \quad (7.46)$$

Thus, the fragile landscape experiences two distinct relaxation modes with a factor of almost 20 difference between their respective relaxation times. The difference between strong and fragile relaxations is even more apparent when plotted on a logarithmic scale, as shown qualitatively in Figure 7.5.

These results give compelling numerical support for the argument of Stillinger and Angell that a strong liquid should have a more uniform potential energy topography than that of a fragile liquid. One final question is whether the strong landscape in Figure 7.1(a) can be made fragile by introducing a distribution of transition energies, such as in Figure 7.6. Figure 7.7 shows that such a landscape does exhibit a high degree of fragility. Thus, a system can be made fragile through non-uniform inherent structure or transition state

energies.

7.4 Conclusions

We have derived a new model of structural relaxation in glass based on nonequilibrium statistical mechanics and the Stillinger model of inherent structures. Using this model and an idealized one-dimensional system, we have numerically demonstrated the connection between the topography of a potential energy landscape and its corresponding fragility. Our model should provide for the accurate computation of glass properties from fundamental physics, accounting for the full effects of both composition and thermal history. Several challenges remain in order to apply our model to a real glass-forming system, most notably the computation of inherent structure and transition state energies for a realistic system in $3N$ -dimensional space. This problem is addressed in the ensuing chapters.

Chapter 8

Eigenvector-Following Technique for Mapping Energy Landscapes

The investigation of energy landscapes is of critical importance to many of the most challenging problems in chemical physics, including the study of molecular clusters,²²²⁻²²⁵ biomolecules,²²⁵ supercooled liquids,^{167,177} and structural glasses.²²⁵⁻²²⁷ An energy landscape itself consists of many peaks and valleys in a multidimensional configuration space. Energy minima correspond to mechanically stable configurations of the system, and are often termed “inherent structures.”¹⁷⁶ Transitions between minima govern such important properties as reaction kinetics, protein folding dynamics, and glass transition range behavior.²²⁵ While it is straightforward to locate energy minima using geometry optimization,^{228,229} the search for transition points has proved much more challenging.^{225,229}

A transition point is formally defined as a stationary point where precisely one of the eigenvalues of the Hessian matrix is negative.²²⁵ Thus, a transition point corresponds

to an energy maximum in one eigendirection and an energy minimum in all other eigendirections. Many methods for finding transition states have been proposed based on an eigenvector-following technique, in which the second derivatives of the energy function are used to construct a Hessian matrix.^{222,225,229–235} The eigenvector-following technique is useful for finding likely transitions from a particular minimum to adjacent minima without having *a priori* knowledge of these neighboring minima. This technique is particularly relevant in kinetic Monte Carlo²³⁶ and other types of dynamic simulations involving energy landscapes.

Previous eigenvector-following methods have employed a Lagrange formalism in order to constrain the walk from an energy minimum to a transition point. While initial techniques employed just a single Lagrange multiplier,^{230–235} a significant improvement by Wales²²² made use of a separate Lagrange multiplier for each eigendirection.

In this chapter, we present an extension of the Wales eigenvector-following technique using a simplified choice of Lagrange multipliers based on rigorous geometrical arguments. We also provide a clear derivation of the eigenvector-following technique in the Lagrange formalism. We then outline an algorithm for implementing our simplified eigenvector-following method and show applications with the two-dimensional Cerjan-Miller²³⁰ and Adams²³⁵ landscapes. The technique is shown to be remarkably robust, even with large step sizes.

8.1 Derivation

Consider a $3N$ -dimensional potential energy landscape,

$$U = U(x_1, x_2, \dots, x_{3N}), \quad (8.1)$$

with the generalized position coordinates $x_1, x_2, \dots, x_{3N}$. If the potential of the system at an initial position x_i^0 , where $i = 1, 2, \dots, 3N$, is given by $U(x_i^0)$, then we may approximate the potential at a new position $x_i = x_i^0 + h_i$ using the Taylor series expansion,

$$U(x_i) \approx U(x_i^0) + \sum_{j=1}^{3N} \left. \frac{\partial U}{\partial x_j} \right|_{x_{i,j}=x_{i,j}^0} h_j + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \left. \frac{\partial^2 U}{\partial x_i \partial x_j} \right|_{x_{i,j}=x_{i,j}^0} h_j. \quad (8.2)$$

This can be written in matrix notation as

$$U(\mathbf{x}) \approx U(\mathbf{x}^0) + \mathbf{g}^\top \mathbf{h} + \frac{1}{2} \mathbf{h}^\top \mathbf{H} \mathbf{h}, \quad (8.3)$$

where the position vectors are given by

$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{3N} \end{pmatrix}; \quad \mathbf{x}^0 = \begin{pmatrix} x_1^0 \\ x_2^0 \\ \vdots \\ x_{3N}^0 \end{pmatrix} \quad (8.4)$$

and the displacement vector $\mathbf{h} = \mathbf{x} - \mathbf{x}^0$ is

$$\mathbf{h} = \begin{pmatrix} h_1 \\ h_2 \\ \vdots \\ h_{3N} \end{pmatrix}. \quad (8.5)$$

The gradient vector $\mathbf{g}$ and $3N \times 3N$ Hessian matrix $\mathbf{H}$, evaluated at $\mathbf{x} = \mathbf{x}^0$, are given by

$$\mathbf{g} = \begin{pmatrix} \frac{\partial U}{\partial x_1} \\ \frac{\partial U}{\partial x_2} \\ \vdots \\ \frac{\partial U}{\partial x_{3N}} \end{pmatrix}_{\mathbf{x}=\mathbf{x}^0} \quad (8.6)$$

and

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 U}{\partial x_1 \partial x_{3N}} \\ \frac{\partial^2 U}{\partial x_2 \partial x_1} & \frac{\partial^2 U}{\partial x_2^2} & \cdots & \frac{\partial^2 U}{\partial x_2 \partial x_{3N}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial x_{3N} \partial x_1} & \frac{\partial^2 U}{\partial x_{3N} \partial x_2} & \cdots & \frac{\partial^2 U}{\partial x_{3N}^2} \end{pmatrix}_{\mathbf{x}=\mathbf{x}^0}, \quad (8.7)$$

respectively. The Hessian matrix is symmetric by construction.

8.1.1 Newton-Raphson Method

In an unconstrained system, the Newton-Raphson method can be used to locate a stationary point in the energy landscape.²²⁸ Based on Equation (8.2), a stationary point must satisfy

$$\frac{\partial U}{\partial h_k} = 0 = \sum_{j=1}^{3N} \left. \frac{\partial U}{\partial x_j} \right|_{x_j=x_j^0} \delta_{jk} + \sum_{i=1}^{3N} \sum_{j=1}^{3N} \delta_{ik} \left. \frac{\partial^2 U}{\partial x_i \partial x_j} \right|_{x_j=x_j^0} h_j, \quad (8.8)$$

or, more compactly,

$$0 = g_k + \sum_{j=1}^{3N} H_{kj} h_j. \quad (8.9)$$

In matrix notation, we have

$$\mathbf{0} = \mathbf{g} + \mathbf{H}\mathbf{h}, \quad (8.10)$$

so that the Newton-Raphson step is given by

$$\mathbf{h} = -\mathbf{H}^{-1}\mathbf{g}. \quad (8.11)$$

We now define b_k and $\mathbf{V}_k$ as the eigenvalues and associated eigenvectors of the symmetric Hessian matrix,

$$\mathbf{H}\mathbf{V}_k = b_k \mathbf{V}_k, \quad (8.12)$$

where the eigenvectors are normalized and satisfy $\mathbf{V}_j^\top \mathbf{V}_k = \delta_{jk}$. Since the eigenvectors $\mathbf{V}_k$ form a complete set, we can express the gradient vector as

$$\mathbf{g} = \sum_{k=1}^{3N} F_k \mathbf{V}_k. \quad (8.13)$$

Substituting this expression into Equation (8.11), we obtain

$$\mathbf{h} = -\mathbf{H}^{-1} \sum_{k=1}^{3N} F_k \mathbf{V}_k \quad (8.14)$$

$$= -\sum_{k=1}^{3N} \frac{F_k}{b_k} \mathbf{V}_k. \quad (8.15)$$

The change in energy after taking the Newton-Raphson step is

$$U(\mathbf{x}) - U(\mathbf{x}^0) = \Delta U = \mathbf{g}^\top \mathbf{h} + \frac{1}{2} \mathbf{h}^\top \mathbf{H} \mathbf{h}. \quad (8.16)$$

Substituting in Equations (8.13) and (8.15), we obtain

$$\Delta U = \left[\sum_{j=1}^{3N} F_j \mathbf{V}_j^\top \right] \left[-\sum_{k=1}^{3N} \frac{F_k}{b_k} \mathbf{V}_k \right] + \frac{1}{2} \left[-\sum_{k=1}^{3N} \frac{F_k}{b_k} \mathbf{V}_k^\top \right] \mathbf{H} \left[-\sum_{j=1}^{3N} \frac{F_j}{b_j} \mathbf{V}_j \right] \quad (8.17)$$

$$= -\sum_{j=1}^{3N} \sum_{k=1}^{3N} \frac{F_j F_k}{b_k} \delta_{jk} + \frac{1}{2} \sum_{j=1}^{3N} \sum_{k=1}^{3N} \frac{F_j F_k}{b_k} \delta_{jk}, \quad (8.18)$$

which simplifies to

$$\Delta U = -\sum_{j=1}^{3N} \frac{F_j^2}{2b_j}. \quad (8.19)$$

Hence, a positive eigenvalue $b_j > 0$ leads to a decrease in energy along the associated $\mathbf{V}_j$ eigendirection, and a negative eigenvalue $b_j < 0$ leads to an increase in energy along its associated eigendirection.

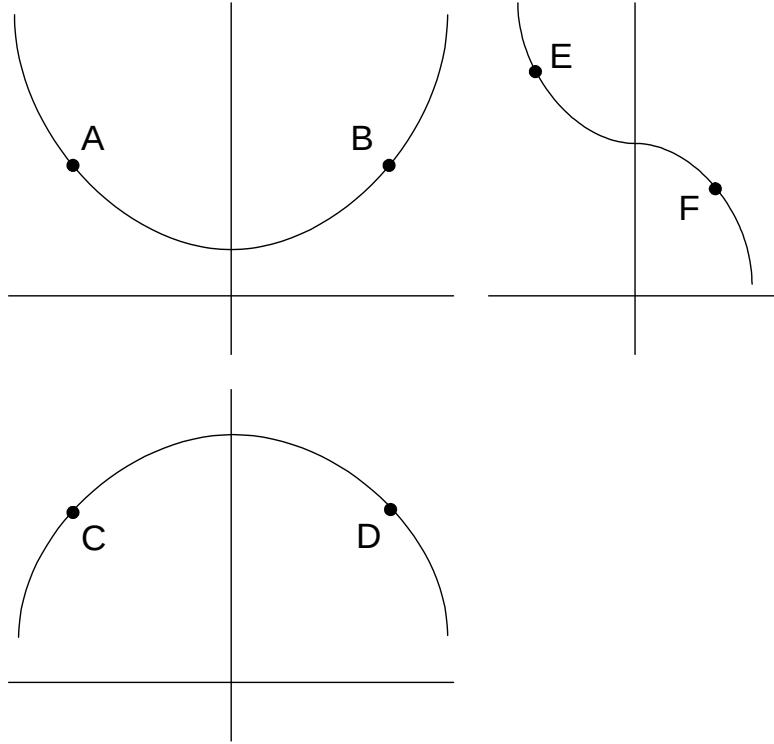


Figure 8.1. Model one-dimensional landscapes. The Newton-Raphson method always drives the system toward a stationary point.

Newton-Raphson in One Dimension

In order to understand the implications of the Newton-Raphson method, let us consider the simple one-dimensional landscapes in Figure 8.1. In one dimension, the Newton-Raphson step in Equation (8.15) simplifies to

$$h = -\frac{F}{b} = -\frac{\frac{\partial U}{\partial x} \Big|_{x=x^0}}{\frac{\partial^2 U}{\partial x^2} \Big|_{x=x^0}}, \quad (8.20)$$

and the change in energy in Equation (8.19) becomes

$$\Delta U = -\frac{F^2}{2b} = -\frac{\left(\frac{\partial U}{\partial x}\bigg|_{x=x^0}\right)^2}{2 \frac{\partial^2 U}{\partial x^2}\bigg|_{x=x^0}}. \quad (8.21)$$

Consider the point A in Figure 8.1, where the gradient $\partial U/\partial x$ is negative and the curvature $\partial^2 U/\partial x^2$ is positive. Based on Equation (8.20), this leads to a positive Newton-Raphson step, $h > 0$, driving the system to the right of A and toward the minimum in energy. Appropriately, the change in energy associated with the Newton-Raphson step, given by Equation (8.21), is negative. If we take a Newton-Raphson step starting from point B, we see that $\partial U/\partial x > 0$ and $\partial^2 U/\partial x^2 > 0$. Hence the Newton-Raphson step from point B is leftward, again driving the system toward the minimum in energy. Hence, the sign of ΔE depends only on the sign of the curvature, $\partial^2 U/\partial x^2$: a positive curvature leads to a decrease in the energy of the system, and a negative curvature leads to an increase in energy.

Performing a similar analysis for points C and D in Figure 8.1, we see the Newton-Raphson step again drives that system toward a stationary point, but in this case it is a maximum rather a minimum in energy. This is in agreement with Equation (8.21), which predicts an increase in energy when starting from a point of negative curvature. Finally, if we consider a step from point E or F, we see that the Newton-Raphson method drives the system toward any type of stationary point—it need not be an absolute minimum or maximum in energy.

8.1.2 Lagrange Approach

A transition point is a stationary point where exactly one eigenvalue of the Hessian matrix $\mathbf{H}$ is negative. In other words, a transition point corresponds to an energy maximum in one direction and an energy minimum in all other directions. Whereas the Newton-Raphson method finds any type of stationary point, we wish to constrain ourselves to just these first-order transition points. Following the approach of Wales,²²² we define the Lagrange function

$$\mathcal{L} = -U(\mathbf{x}) + \frac{1}{2} \sum_{i=1}^{3N} \lambda_i (h_i^2 - c_i^2) \quad (8.22)$$

$$\begin{aligned} &= -U(x_i^0) - \sum_{j=1}^{3N} \left. \frac{\partial U}{\partial x_j} \right|_{x_j=x_j^0} h_j - \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \left. \frac{\partial^2 U}{\partial x_i \partial x_j} \right|_{x_j=x_j^0} h_j + \\ &\quad \frac{1}{2} \sum_{i=1}^{3N} \lambda_i (h_i^2 - c_i^2), \end{aligned} \quad (8.23)$$

where c_i are the desired step sizes in the various directions and λ_i are Lagrange multipliers.

Taking the derivative of $\mathcal{L}$ with respect to an arbitrary step h_k , we obtain

$$\frac{\partial \mathcal{L}}{\partial h_k} = 0 = - \sum_{j=1}^{3N} \left. \frac{\partial U}{\partial x_j} \right|_{x_j=x_j^0} \delta_{jk} - \sum_{i=1}^{3N} \sum_{j=1}^{3N} \delta_{ik} \left. \frac{\partial^2 U}{\partial x_i \partial x_j} \right|_{x_j=x_j^0} h_j + \sum_{i=1}^{3N} \lambda_i h_i \delta_{ik}, \quad (8.24)$$

which simplifies to

$$0 = -g_k - \sum_{j=1}^{3N} H_{kj} h_j + \lambda_k h_k. \quad (8.25)$$

In matrix notation, we have

$$\mathbf{0} = -\mathbf{g} - \mathbf{H}\mathbf{h} + \boldsymbol{\lambda}\mathbf{h}, \quad (8.26)$$

where $\boldsymbol{\lambda}$ is a diagonal matrix given by

$$\boldsymbol{\lambda} = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \lambda_N \end{pmatrix}. \quad (8.27)$$

Solving for $\mathbf{h}$ in Equation (8.26) we have

$$\mathbf{h} = (\boldsymbol{\lambda} - \mathbf{H})^{-1} \mathbf{g}, \quad (8.28)$$

and substituting Equation (8.13) for the gradient, we obtain

$$\mathbf{h} = (\boldsymbol{\lambda} - \mathbf{H})^{-1} \sum_{k=1}^{3N} F_k \mathbf{V}_k. \quad (8.29)$$

Thus, the Lagrange step is given by

$$\mathbf{h} = \sum_{k=1}^{3N} \frac{F_k}{\lambda_k - b_k} \mathbf{V}_k. \quad (8.30)$$

The associated change in energy is

$$\Delta U = \mathbf{g}^\top \mathbf{h} + \frac{1}{2} \mathbf{h}^\top \mathbf{H} \mathbf{h} \quad (8.31)$$

$$\begin{aligned} &= \left[\sum_{j=1}^{3N} F_j \mathbf{V}_j^\top \right] \left[\sum_{k=1}^{3N} \frac{F_k}{\lambda_k - b_k} \mathbf{V}_k \right] + \\ &\quad \frac{1}{2} \left[\sum_{k=1}^{3N} \frac{F_k}{\lambda_k - b_k} \mathbf{V}_k^\top \right] \mathbf{H} \left[\sum_{j=1}^{3N} \frac{F_j}{\lambda_j - b_j} \mathbf{V}_j \right], \end{aligned} \quad (8.32)$$

which simplifies to

$$\Delta U = \sum_{j=1}^{3N} \frac{F_j^2}{\lambda_j - b_j} + \frac{1}{2} \sum_{j=1}^{3N} \frac{F_j^2 b_j}{(\lambda_j - b_j)^2} \quad (8.33)$$

$$= \sum_{j=1}^{3N} \frac{F_j^2 \left(\lambda_j - \frac{b_j}{2} \right)}{(\lambda_j - b_j)^2}. \quad (8.34)$$

Hence, the sign of the energy change in a particular eigendirection $\mathbf{V}_j$ depends on both the eigenvalue b_j and the choice of Lagrange multiplier λ_j .

Lagrange Approach in One Dimension

Let us again consider the simple one-dimensional landscapes in Figure 8.1 in order to understand the role of the Lagrange multipliers in Equations (8.30) and (8.34). In one dimension, these equations reduce to

$$h = \frac{F}{\lambda - b} = \frac{\frac{\partial U}{\partial x} \Big|_{x=x^0}}{\lambda - \frac{\partial^2 U}{\partial x^2} \Big|_{x=x^0}}, \quad (8.35)$$

and

$$\Delta U = \frac{F^2 \left(\lambda - \frac{b}{2} \right)}{(\lambda - b)^2} = \frac{F^2 \left(\lambda - \frac{1}{2} \frac{\partial^2 U}{\partial x^2} \Big|_{x=x^0} \right)}{\left(\lambda - \frac{\partial^2 U}{\partial x^2} \Big|_{x=x^0} \right)^2}. \quad (8.36)$$

If we want to minimize energy, then $\lambda - b/2 < 0$, or $\lambda < b/2$. Starting from point A, we wish to have $h > 0$ in order to move in the appropriate direction. Since the gradient is negative at this point, Equation (8.35) leads to the condition $\lambda - b < 0$, or $\lambda < b$. Since $b > 0$ at point A, we must therefore choose $\lambda < b/2$ in order to satisfy both conditions.

Let us now suppose that we wish to minimize energy starting from point B. The same condition, $\lambda < b/2$, holds from Equation (8.36). From Equation (8.35), we have the condition $\lambda < b$ since $F > 0$ and we wish to have $h < 0$ from this point. Since we are still in the regime of $b > 0$, we must again choose $\lambda < b/2$ in order to both decrease energy and move in the leftward direction. Hence, the condition $\lambda < b/2$ for energy minimization is the same for both points A and B.

Suppose now that we wish to maximize energy starting from point A. From Equation (8.35), we have $\lambda - b/2 > 0$, or $\lambda > b/2$. From Equation (8.35), we have $\lambda - b > 0$, or $\lambda > b$. Since $b > 0$, we must have the condition $\lambda > b$. A similar analysis starting from point B gives the same result.

Now let us consider points C and D, where $b < 0$. For energy minimization we obtain the condition $\lambda < b$, and for energy maximization we have $\lambda > b/2$. Thus, for any arbitrary value of b , we may walk “downhill” on the energy landscape with $\lambda < -|b|$ and “uphill” with $\lambda > |b|$.

A Simplified Choice of Lagrange Multipliers

Let us now return to our N -dimensional energy landscape. We may rewrite Equation (8.34) as a summation of energy changes in the various eigendirections:

$$\Delta U = \sum_{j=1}^{3N} \Delta U_j, \quad (8.37)$$

where

$$\Delta U_j = \frac{F_j^2 \left(\lambda_j - \frac{b_j}{2} \right)}{(\lambda_j - b_j)^2}. \quad (8.38)$$

Suppose we wish to find a transition point by maximizing energy in a particular $\mathbf{V}_i$ direction while minimizing energy in all of the orthogonal $\mathbf{V}_{j \neq i}$ directions. It follows from our analysis in Section 8.1.2 that a choice of $\lambda_i > |b_i|$ and $\lambda_j < -|b_j|$ would guarantee a step in the correct direction. However, it specifies neither the particular values of $\lambda_{i,j}$ nor the magnitude of the step.

We may simplify our analysis by assuming that a transition point search always starts from a local minimum in the energy landscape. This is also the most practical case to consider from an applications point of view, since we are typically interested in finding the transition energy between two stable configurations, e.g., “reactant” and “product” in chemical kinetics or two “inherent structures” using Stillinger’s terminology.¹⁷⁶ A minimum in the potential energy landscape has the property $b_k > 0$ for all $k = 1, 2, \dots, N$. As we walk on the potential energy landscape from the minimum to a transition point, we are essentially walking uphill along a “valley” or “streambed.” If the direction of our walk up the streambed is $\mathbf{V}_i$ and the step size is sufficiently small, we should have $b_j > 0$ for all

$j \neq i$ and be near the energy minima in the $\mathbf{V}_{j \neq i}$ directions along the entire walk. In the case of an infinitesimal step size, we would exactly follow the streambed; however, due to finite step sizes, we may have slight deviations from the streambed. These deviations may be corrected by an appropriate choice of $\lambda_{j \neq i}$, which is accomplished by finding the nearest stationary point in the $\Delta E_{j \neq i}$ contribution:

$$\frac{\partial \Delta U_{j \neq i}}{\partial \lambda_{j \neq i}} = 0 = -\frac{2F_{j \neq i}^2}{(\lambda_{j \neq i} - b_{j \neq i})^3} \left(\lambda_{j \neq i} - \frac{b_{j \neq i}}{2} \right) + \frac{F_{j \neq i}^2}{(\lambda_{j \neq i} - b_{j \neq i})^2}, \quad (8.39)$$

leading to

$$\frac{2 \left(\lambda_{j \neq i} - \frac{b_{j \neq i}}{2} \right)}{\lambda_{j \neq i} - b_{j \neq i}} = 1. \quad (8.40)$$

Therefore, we have

$$\lambda_{j \neq i} = 0. \quad (8.41)$$

The choice of $\lambda_{j \neq i} = 0$ reduces our Lagrange approach to exactly the Newton-Raphson method in all $\mathbf{V}_{j \neq i}$ eigendirections, and it is in agreement with our previous condition of $\lambda_{j \neq i} < b_{j \neq i}/2$ for energy minimization with $b_{j \neq i} > 0$. Note that if we accidentally step outside of the regime where $b_{j \neq i} > 0$, a negative $\lambda_{j \neq i} < b_{j \neq i}$ should be chosen. (This also indicates that the chosen step size in the $\mathbf{V}_i$ eigendirection is too large—so large that we have effectively stepped out of the streambed and started climbing hills in an orthogonal direction.)

The magnitude of the step size along the $\mathbf{V}_i$ eigendirection is given by

$$h_i^2 = c_i^2 = \frac{F_i^2}{(\lambda_i - b_i)^2}. \quad (8.42)$$

This leads to the condition

$$\lambda_i = b_i \pm \left| \frac{F_i}{c_i} \right|. \quad (8.43)$$

Since $\lambda_i > b_i$ is required for energy maximization with $b_i > 0$, we choose

$$\lambda_i = b_i + \left| \frac{F_i}{c_i} \right| \quad (8.44)$$

for this case. This is also the appropriate choice of λ_i for $b_i = 0$. The step sizes $c_{j \neq i}$ in the other directions are fixed by $c_{j \neq i} = |F_j/b_j|$. The total step size is thus

$$\mathbf{h}^\top \mathbf{h} = \frac{F_i^2}{(\lambda_i - b_i)^2} + \sum_{j=1, j \neq i}^{3N} \frac{F_j^2}{b_j^2}. \quad (8.45)$$

If we are close to the energy minima in the $\mathbf{V}_{j \neq i}$ eigendirections, then $F_{j \neq i} \approx 0$ such that

$$\mathbf{h}^\top \mathbf{h} \approx \frac{F_i^2}{(\lambda_i - b_i)^2} = c_i^2. \quad (8.46)$$

Any deviation from $\mathbf{h}^\top \mathbf{h} = c_i^2$ is a result of having finite values of $F_{i \neq j}^2$.

As we progress up the streambed, eventually we will pass through an inflection point where b_i becomes negative. The condition for energy maximization with $b_i < 0$ is $\lambda_i > b_i/2$. Since in this case the nearest stationary point is the transition point of interest with exactly one negative eigenvalue b_i , the most efficient choice of Lagrange multiplier is $\lambda_i = 0$, corresponding again to the Newton-Raphson step of Equation (8.15). Thus in the case of $b_i < 0$, the step size c_i is determined by the Newton-Raphson method.

Finally, we note that the first step from the initial minimum point must follow a

different scheme than that given by Equation (8.42) since $F_i = 0$. In this case, we choose a simple step of magnitude c_i in the $\mathbf{V}_i$ eigendirection. There should be no components of $\mathbf{h}$ in the other $\mathbf{V}_{j \neq i}$ eigendirections since we also have $F_{j \neq i} = 0$ and wish to remain in the streambed.

8.2 Algorithm

We now provide an algorithm for implementing the above Lagrange approach for finding transition states.

1. Find a local minimum in the potential energy landscape using steepest descent or another geometry optimization method.^{225,228} Compute the Hessian matrix and determine its eigenvalues and normalized eigenvectors. Choose the eigenvector $\mathbf{V}_i$ corresponding to the direction of interest, typically that of the “softest mode,” i.e., that corresponding to the smallest eigenvalue. Higher-order modes can be chosen to locate other transition states adjacent to the current energy minimum. These transition points are likely to be of higher energy than that corresponding to the softest mode.
2. Step in the direction of the eigenvector $\mathbf{V}_i$ of interest using a desired magnitude c_i . This initial step $\mathbf{h}$ should have no components from the other $\mathbf{V}_{j \neq i}$ eigendirections. When mapping out a complete list of transition points, a second search should be initiated in the opposite $-\mathbf{V}_i$ direction.
3. Compute the gradient $\mathbf{g}$ and Hessian $\mathbf{H}$ at the new point, and determine the eigenval-

ues and normalized eigenvectors of the new Hessian matrix. The eigenvectors form the columns of a $3N \times 3N$ unitary matrix:

$$\mathbf{U} = \begin{pmatrix} \mathbf{V}_1 & \mathbf{V}_2 & \cdots & \mathbf{V}_{3N} \end{pmatrix}. \quad (8.47)$$

4. Compute the vector $\mathbf{F} = \mathbf{U}^\top \mathbf{g}$, where

$$\mathbf{F} = \begin{pmatrix} F_1 \\ F_2 \\ \vdots \\ F_{3N} \end{pmatrix}. \quad (8.48)$$

5. Choose the eigenvalue b_i of interest, typically the smallest.
6. If the magnitude of b_i is less than some threshold b_{th} , then we are near an inflection point in U . In this regime, our step should be dominated by the first derivative of U , e.g., the gradient vector. Determine the largest value of F_k and its corresponding eigenvector $\mathbf{V}_k$. Step in the direction of $\mathbf{V}_k$ along the upward gradient using a desired magnitude c_k . This displacement should have no contributions from the other $\mathbf{V}_{j \neq k}$ eigendirections. Proceed to step 9.
7. If $|b_i| > b_{th}$, choose the eigenvector $\mathbf{V}_i$ corresponding to b_i . Set the Lagrange multipliers $\lambda_{j \neq i} = 0$ corresponding to the Newton-Raphson step for all directions orthogonal to $\mathbf{V}_i$. If $b_i \geq 0$, choose $\lambda_i = b_i + |F_i/c_i|$, where c_i is the desired step size in the $\mathbf{V}_i$ direction. If $b_i < 0$, choose $\lambda_i = 0$. (Note that the choice of $\lambda_{j \neq i} = 0$ assumes that

we are sufficiently close to the “streambed” of the potential energy landscape such that $b_{j \neq i} > 0$. If $b_{j \neq i} \leq 0$, the desired step size c_i is probably too large. This can be corrected by either choosing a smaller value of c_i or by choosing $\lambda_{j \neq i} < b_{j \neq i}$.)

8. Compute the step

$$\mathbf{h} = \sum_{k=1}^N \frac{F_k}{\lambda_k - b_k} \mathbf{V}_k, \quad (8.49)$$

and update the system coordinates appropriately.

9. Repeat steps 3-8 until converged at a transition point. The criterion for convergence is $|F_i| < \epsilon$, where ϵ is chosen to reflect the desired level of precision.

We note that some previous techniques have incorporated a dynamically variable maximum step size, which may be combined with a trust radius.²²⁵ In our algorithm, the step size in the $b_i \geq 0$ regime is controlled by the c_i parameter, which is user-definable. However, in the $b_i < 0$ regime the step size is governed entirely by the values of F_i and b_i in order to choose an optimum step toward the transition point. We also note that for large atomistic systems, it may be undesirable to compute or diagonalize the Hessian matrix. In this case, hybrid techniques exist for estimating the smallest Hessian eigenvalues and corresponding eigenvectors.²²⁵

One final consideration for atomistic systems is that translation or rotation of the entire simulation cell leads to zero Hessian eigenvalues, making inversion of the Hessian matrix impossible. However, this problem may be avoided by either changing to a minimal set of internal coordinates²²⁵ or using an eigenvalue-eigenvector solver that does not rely on explicit matrix inversion, such as the excellent Template Numerical Toolkit.²³⁷

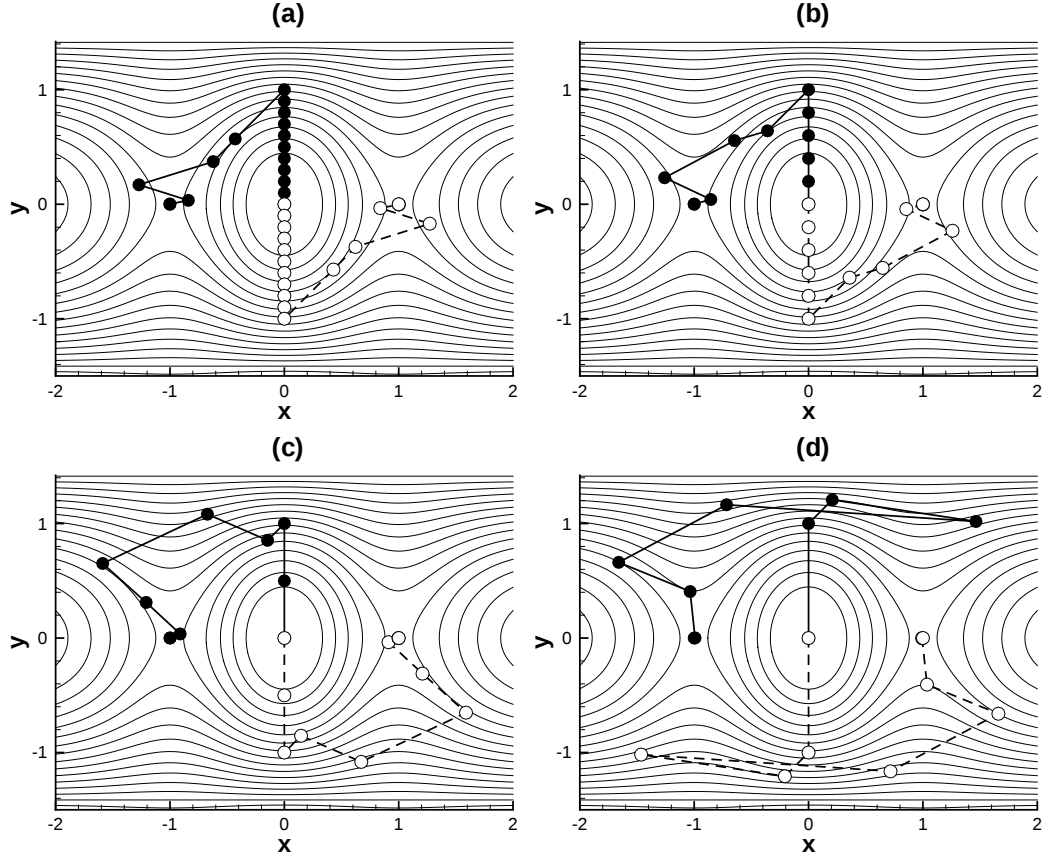


Figure 8.2. Contour plot of the two-dimensional Cerjan-Miller function of Equation (8.50), using $a = 1$, $b = \frac{1}{2}$, and $c = 1$. Starting from the minimum at $(x, y) = (0, 0)$, we find the transition points at $(\pm 1, 0)$ using a step size of (a) 0.1, (b) 0.2, (c) 0.5, and (d) 1.0. Solid lines indicate an initial step in the $+y$ direction, and dashed lines indicate an initial step in the $-y$ direction.

8.3 Examples

As a first example of the above algorithm, let us consider the two-dimensional Cerjan-Miller energy function,²³⁰

$$U_{CM}(x, y) = (a - by^2)x^2e^{-x^2} + \frac{c}{2}y^2. \quad (8.50)$$

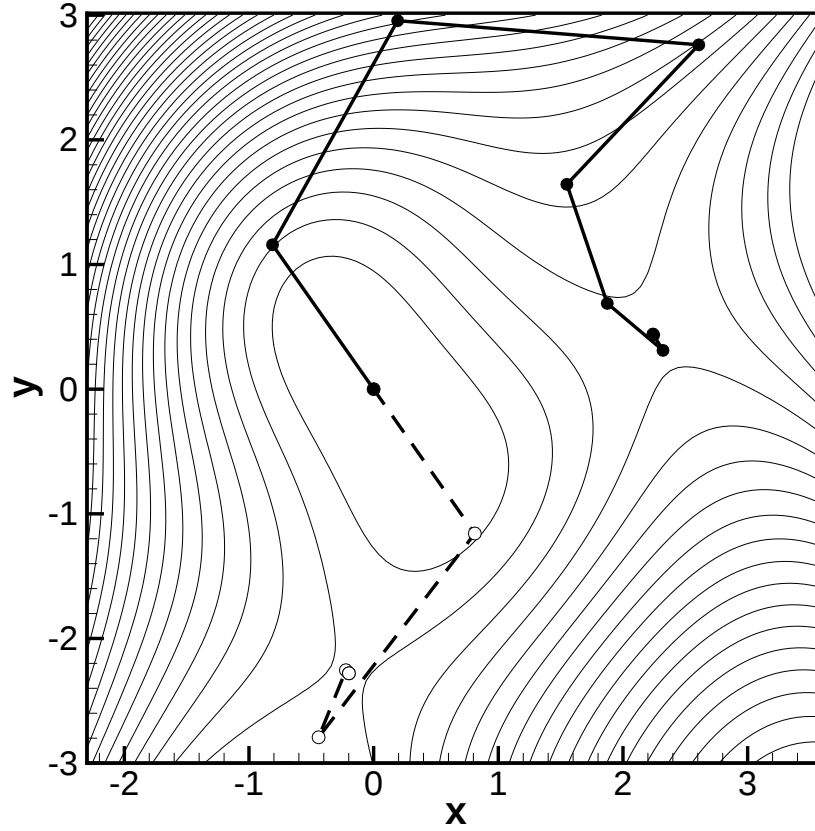


Figure 8.3. Contour plot of the two-dimensional Adams function of Equation (8.51). Starting from the minimum at $(x, y) = (0, 0)$, we find the two transition points at $(2.4104, 0.4419)$ and $(-0.1985, -2.2793)$. The initial step size is chosen to be 2.0, and the initial step is taken in opposite directions along the softest mode.

The minimum energy is located at the origin, and the two transition points are located symmetrically at $(x, y) = (\pm 1, 0)$. In order to provide a difficult test for our algorithm, we choose $a = 1$, $b = \frac{1}{2}$, and $c = 1$, which gives the softest mode in the y direction. Figure 8.2 shows a contour plot of the Cerjan-Miller function with transition point searches shown for four different step sizes: 0.1, 0.2, 0.5, and 1.0. Choosing an initial step in the $+y$ direction, all four cases converge upon the left transition point at $(-1, 0)$. If the opposite $-y$ direction is chosen for the initial step, then the algorithm converges symmetrically to

the right transition point at $(1, 0)$. Figure 8.2 shows that a shorter step size leads to a more direct path to the transition point, but it can be less efficient since a greater number of steps are required. The fact that even the relatively large step size of 1.0 leads to convergence illustrates the robustness of the algorithm, even when the initial step is chosen in what is essentially the “wrong” direction. Note that in all four cases shown in Figure 8.2, the step size is determined solely by the Newton-Raphson method after leaving the regime where $b_i \geq 0$.

For a second example, we consider the Adams function,²³⁵

$$U_A(x, y) = 2x^2(4 - x) + y^2(4 + y) - xy \left[6 - 17e^{-\frac{1}{4}(x^2 + y^2)} \right]. \quad (8.51)$$

Starting from the minimum at the origin, we locate the two transition points at $(2.4104, 0.4419)$ and $(-0.1985, -2.2793)$. Results are shown in Figure 8.3 using an initial step size of 2.0. The two transition points are found by starting in opposite directions along the softest mode. The first transition point at $(2.4104, 0.4419)$ is found in seven steps, and the second transition point at $(-0.1985, -2.2793)$ is found in only four steps, a vast improvement over prior eigenvector-following techniques.²³⁵

8.4 Conclusions

We have derived an eigenvector-following technique for locating transition points in an energy landscape. Our method is based on maximizing energy in one eigendirection of interest while simultaneously minimizing energy in all orthogonal directions. We have outlined an algorithm for implementation of this technique and demonstrated its robustness

using the two-dimensional Cerjan-Miller landscape. This method for locating transition points should be useful in computing reaction kinetics and transition probabilities in a wide range of fields, including the study of molecular clusters, biomolecules, and structural glasses.

Chapter 9

Potential Energy Landscapes of Chalcogen Clusters

The investigation of potential energy landscapes is of critical importance to many of the most challenging problems in chemical physics, including the study of molecular clusters,^{222–225} biomolecules,²²⁵ supercooled liquids,^{167,177} and structural glasses.^{225–227} The potential energy of a system of N particles can be written in terms of a $3N$ -dimensional hypersurface,

$$U = U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (9.1)$$

where $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \in \Re^{3N}$ are the position vectors of the N particles. The U hypersurface itself contains a multitude of local minima, each of which corresponds to a mechanically stable configuration of the system, termed an “inherent structure.”¹⁷⁶ The set of $3N$ -dimensional hyperspace configurations that “drains” to a particular minimum via steepest descent is known as a “basin.”¹⁷⁶ The study of a potential energy landscape

is facilitated by mapping the continuous U hypersurface to a discrete set of minima $\{\alpha\}$. Thus, basins are mapped to their corresponding inherent structures: $\Re^{3N} \rightarrow \{\alpha\}$.

In this chapter, we describe the potential energy landscapes of small chalcogen clusters (Se_3 - Se_8 , $\text{S}_n\text{Se}_{8-n}$, and $\text{Se}_n\text{Te}_{8-n}$) using the eigenvector-following technique derived in Chapter 8. We employ the *ab initio* potentials from Part I of this thesis, which include two-, three-, and effective four-body interactions and have been shown to provide a very good description of chalcogenide glass structure. Following the approach of Becker and Karplus,²³⁸ we construct disconnectivity graphs showing the potential energy minima and transition states of the chalcogen clusters. The disconnectivity graphs are labeled to show the associated configurations of the inherent structures and transition states. Finally, we comment on the relationships between the underlying interatomic potentials and the resulting inherent structures.

9.1 Traversing the Landscape

Thorough mapping of a potential energy landscape involves locating both minima and the intermediate transition points. We employ a recursive procedure for traversing the energy landscape, as depicting by the flow chart in Figure 9.1. First, an initial minimum is found using steepest descent. Then, our eigenvector-following technique is used to locate transition points in the positive and negative eigendirections of the eigenmodes of interest. In this work, we use a step size of $c_i = 0.025 \text{ \AA}$, a gradient tolerance of $\epsilon = 0.001 \text{ eV/\AA}$, and an eigenvalue threshold of $b_{th} = 0.01 \text{ eV/\AA}^2$. We search for transition states recursively from each minimum along the positive and negative eigendirections of the four softest modes.

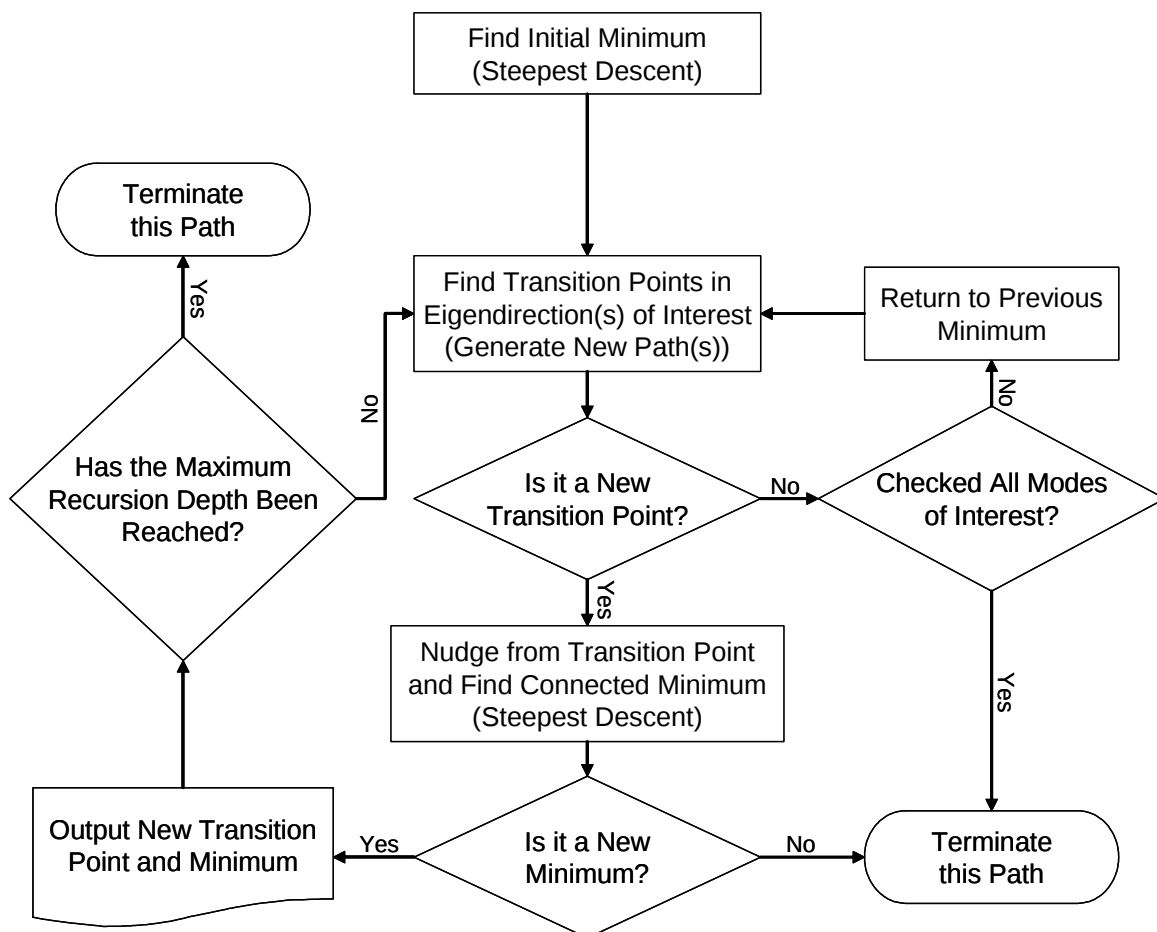


Figure 9.1. Flow chart of the recursive algorithm for traversing a potential energy landscape.

Transition points are typically located within about 30 steps from a given minimum. The recursion depth is varied in order to find more or fewer transition states and minima. The recursive paths of traversal through the landscape are terminated when encountering a minimum or transition point that has already been found or when the maximum recursion depth has been reached for a given path.

We construct the disconnectivity graph for a given cluster using the minimum recursion depth that appropriately captures the various inherent structures of the clusters.

The resulting disconnectivity graph is “pruned” to remove many of the degeneracies that inevitably result when mapping the potential energy landscapes of atomic clusters. Emphasis is placed on the lower-energy inherent structures and their corresponding transition states. Disconnectivity graphs are generated using software by Mark A. Miller,²³⁹ and molecular structures are plotted with XCrysDen²⁴⁰ using the color key in Table XIV.

9.2 Mapping of Small Selenium Clusters (Se₃-Se₇)

We map the potential energy landscapes of Se₃-Se₈ clusters using the above algorithm together with our *ab initio* potentials from Part I. Plots of the two- and three-body interaction potentials are shown in Figures 9.2 and 9.3. A complete description of these potentials can be found in Part I.

9.2.1 Se₃

The potential energy landscape of the Se₃ cluster provides a good introduction to the concept of a disconnectivity graph. The left-hand side of Figure 9.4 shows the total interaction potential of Se₃ as a continuous function of bond angle, assuming an equilibrium separation distance of 2.1735 Å between two pairs of atoms. In such a small cluster, it may be possible to identify all of the inherent structures and transition states from a continuous potential energy function. In the case of Se₃ there are three local minima, labeled A, C, and E, corresponding to the three inherent structures of the cluster. The global minimum occurs at point C and corresponds to a bond angle of about 117°. The potential energy function itself is very shallow around this minimum, allowing for a high degree of bond

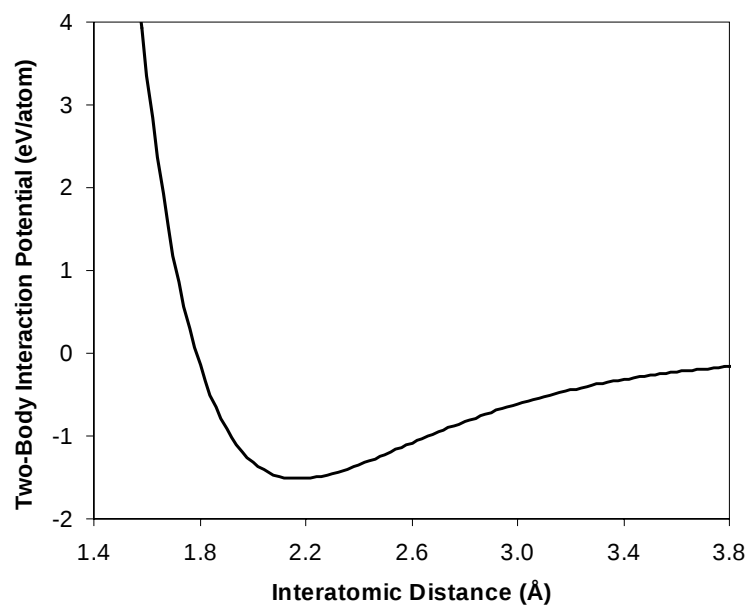


Figure 9.2. Two-body interaction potential for selenium.

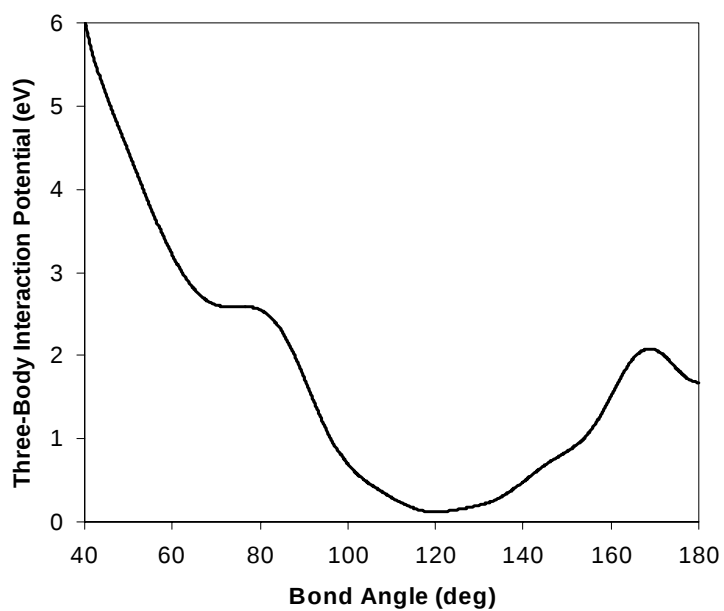


Figure 9.3. Three-body interaction potential for selenium as a function of bond angle, assuming an equilibrium separation distance of 2.1735 Å between two pairs of atoms.

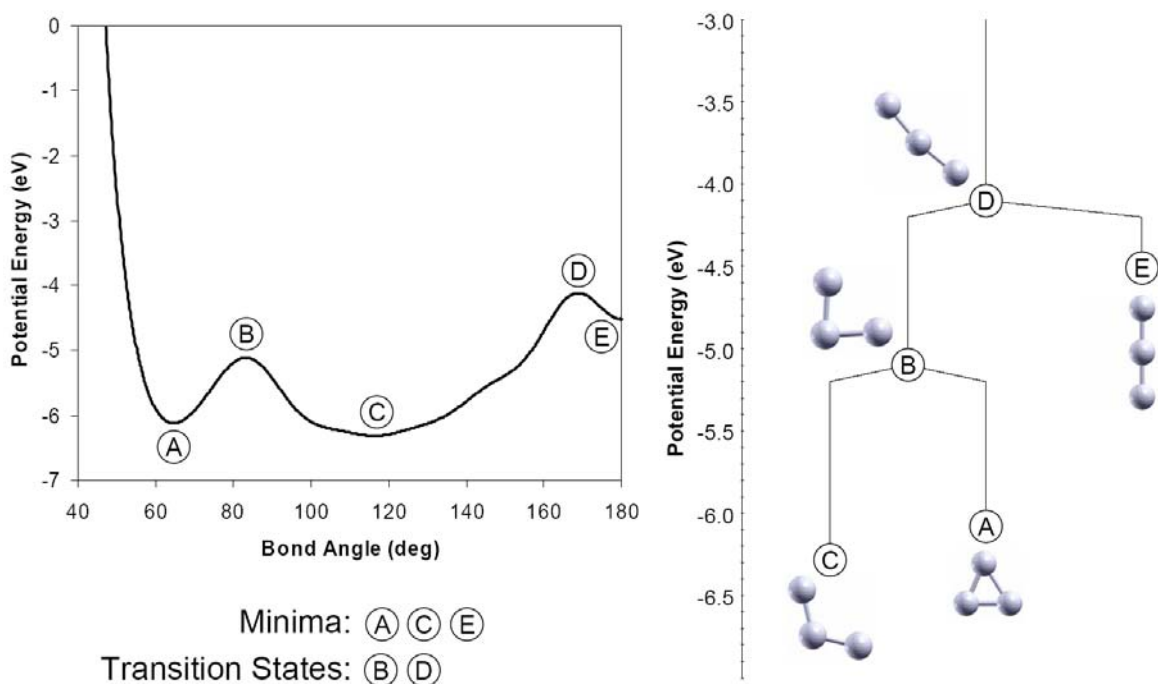


Figure 9.4. Potential energy landscape of the Se_3 cluster. The left-hand side shows potential energy plotted as a continuous function of bond angle, and the right-hand side shows the corresponding disconnectivity graph.

flexibility. A second minimum, of slightly higher energy, occurs at point A around 65° . This corresponds to a closed, triangular configuration of atoms. The third local minimum at point E has a much higher energy and corresponds to a straight-line configuration. The Se_3 cluster has two transition points: one between A and C and the other between C and E. The former, labeled B, occurs at a bond angle of 84° , and the latter transition point, labeled D, occurs at about 169° .

The corresponding disconnectivity graph for Se_3 is shown on the right-hand side of Figure 9.4. The vertical axis gives the potential energy of the system, and the horizontal axis refers to an arbitrary configuration space. The three minima of Se_3 are represented by the terminal nodes, A, C, and E, placed at their corresponding energy levels. The horizontal

positioning of the nodes is arbitrary and chosen to show clearly the connections between the various minima. These connections are provided by the transition nodes, B and D. Transition node B connects minima A and C, and transition node D connects minimum E collectively with A and C.

A disconnectivity graph has the advantage of allowing for a clear description of inherent structures and transition states without having to plot in full $3N$ -dimensional space. Disconnectivity graphs are also useful for determining what transitions are possible with different levels of total energy. For example, if our Se_3 cluster in Figure 9.4 has -5.5 eV of energy, it must be in either of the basins corresponding to minima A or C. Since this amount of energy is less than that of transition point B, a transition between basins A and C would not be possible. On the other hand, if the Se_3 cluster has a total energy of -4.3 eV (between points D and E), the system may occupy any of the three basins, with transitions freely allowed between the A and C basins.

The existence of both open and closed triangular structures for Se_3 is in good agreement with experimental cluster measurements.^{14,241} However, existence of the straight-line configuration E has not been seen experimentally. This is not surprising since it occurs at a much higher energy than both A and C; moreover, the adjacent transition point D has only slightly higher potential than E. Thus, configuration E should be a very short-lived structure. The previous semi-empirical modeling of Oligschleger¹⁴ identified the inherent structures A and C, but not E. Oligschleger *et al.* did not identify the transition points in Se_3 or any of the other selenium clusters since their primary interest was in the configurations of the overall minima.

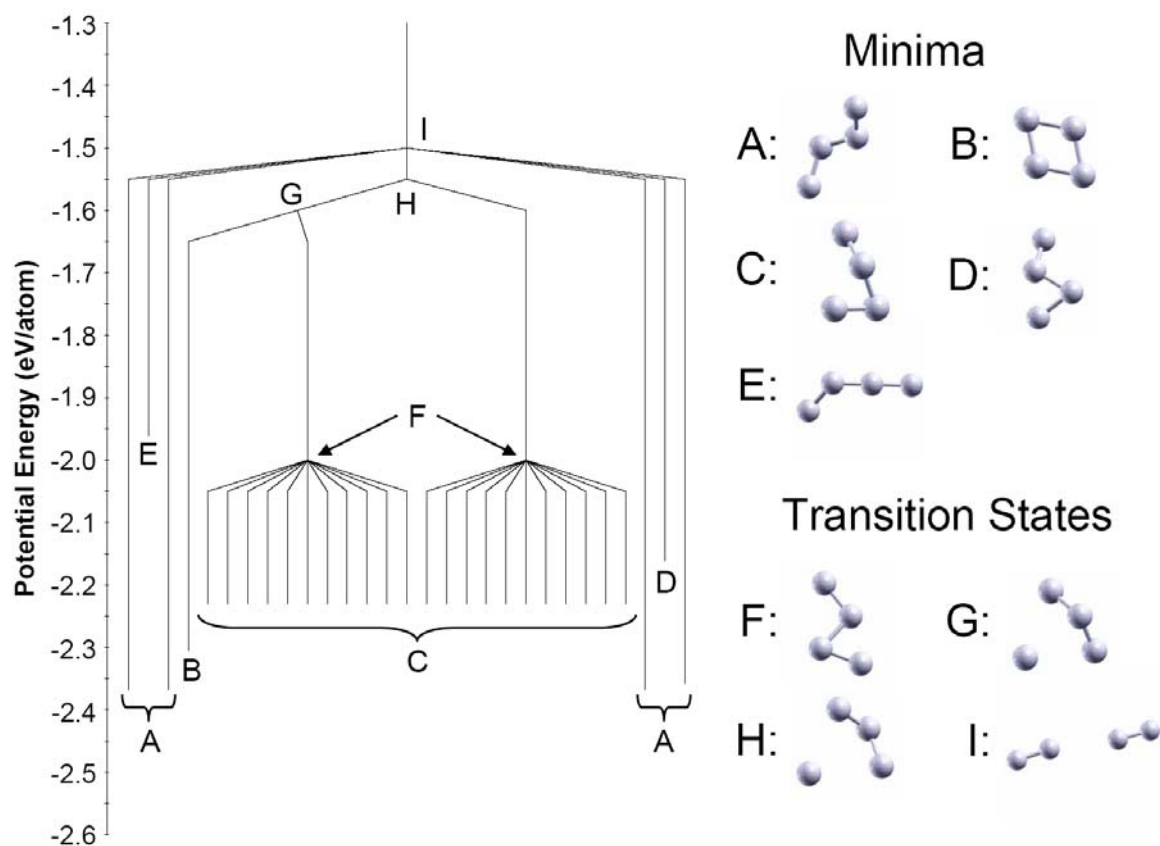


Figure 9.5. Disconnectivity graph for Se_4 and plots of the identified minimum energy structures and transition states.

9.2.2 Se_4

As indicated by the disconnectivity graph in Figure 9.5, the potential energy landscape of Se_4 has a much richer topography than that of Se_3 . The global minimum A is a kinked chain of four selenium atoms with bond angles of about 117° . There are multiple points A in the disconnectivity graph, indicating a high number of degenerate structures with this configuration. The inherent structure with the second-lowest potential energy is the closed configuration of point B, a parallelogram with interior angles of about 65° and 115° . The higher-energy inherent structures consist of chains incorporating increasingly

less favorable bond angles. Inherent structure C, occurring with a high degree of degeneracy, is a four-atom chain with one bond angle of 117° and the other of 65° ; the dihedral angle is 108° . Point D is a variation on this theme, with a slightly less favorable dihedral angle of 132° . Point E is another variation, this time incorporating a less favorable 180° bond angle. The degeneracies of D and E have been suppressed in the disconnectivity graph, as have other higher energy minima (such as a straight-line configuration of all four atoms).

Transitions between degenerate states C can be accomplished by a change in dihedral angle to 180° , as indicated by point F in Figure 9.5. However, in order to switch the 65° and 117° bonds of inherent structure C, i.e., to go between the two sets of degenerate minima in the disconnectivity graph, the system must pass through transition point H, which involves breaking one of the bonds. (It is a lower activation barrier to break one of the bonds than to change bond angles while remaining fully bonded.) The C structure can transition into a parallelogram by passing through transition point G, which also involves breaking one bond. All other transitions occur through point I, which involves breaking the single Se_4 cluster into two Se_2 clusters. It is interesting to note that even transitions between degenerate A minima involve bond breakage. Thus, it is much easier to transition among the various C degenerate structures than those corresponding to the global minimum A.

There is little experimental data on the structure of Se_4 clusters. The semi-empirical modeling of Oligschleger¹⁴ predicts a square as the minimum energy configuration. However, the more realistic *ab initio* potentials for selenium predict the parallelogram of

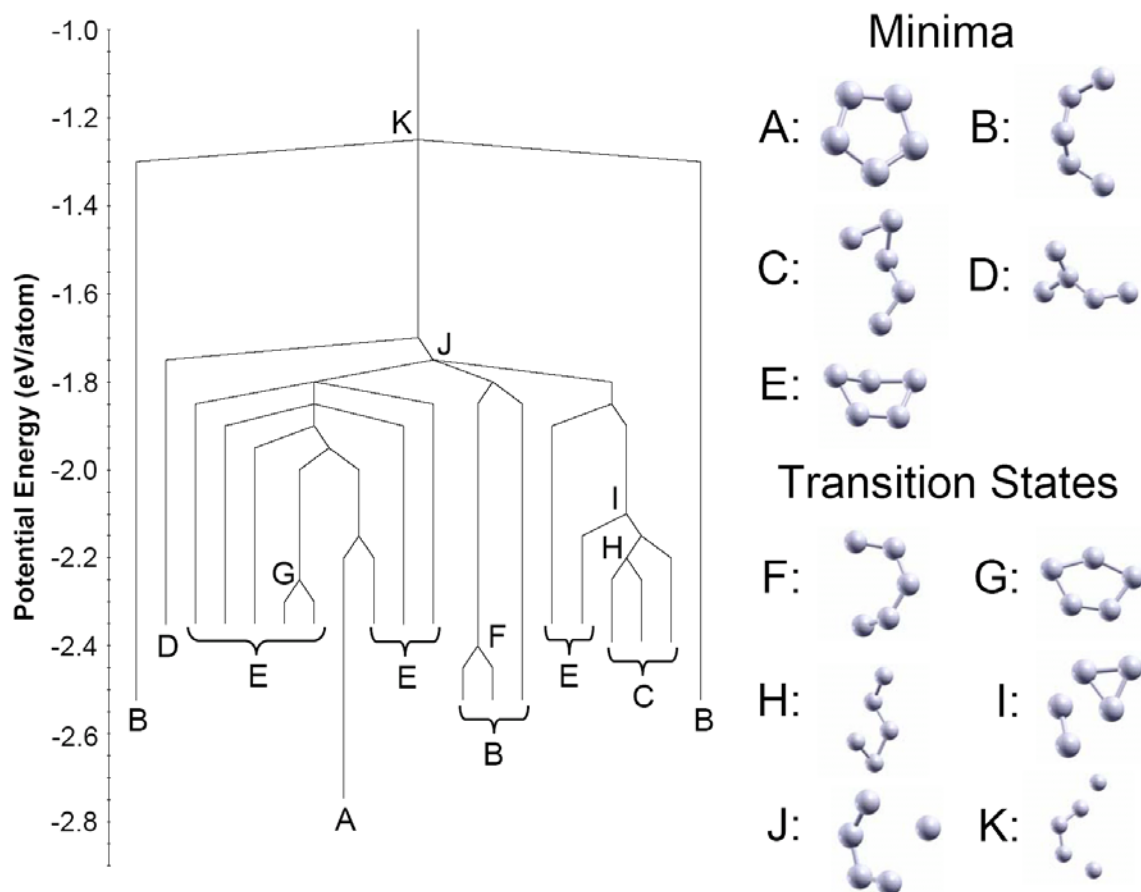


Figure 9.6. Disconnectivity graph for Se_5 and plots of the identified minimum energy structures and transition states.

point B in Figure 9.5, which incorporates more favorable bond angles. Moreover, our global minimum is found to be not a closed configuration, but rather a chain with bond angles of 117° . The energy cost of having one less bond in the chain configuration is more than offset by allowing all of the bond angles to assume the most favorable value of 117° .

9.2.3 Se_5

As shown in Figure 9.6, the global minimum of Se_5 is a regular pentagon corresponding to point A in the disconnectivity graph. The interior bond angles of 108° are

near the shallow minimum of 117° , shown in Figure 9.4 for the three-body cluster. The second most favorable inherent structure of Se_5 is the open chain configuration **B** in Figure 9.6, with all bond angles equal to 117° . As with other chain configurations, **B** has a high degree of degeneracy. The next most favorable configuration, labeled **C**, is a five-atom chain incorporating one 65° and two 117° angles. Other chain structures are also possible but have a significantly higher potential energy. For clarity, these have been omitted from the disconnectivity graph in Figure 9.6.

Inherent structures **D** and **E** have nearly identical energy. Structure **D** involves one three-coordinated selenium atom, with all bond angles equal to 117° . Point **E** is the “envelope” geometry proposed by Oligschleger¹⁴ as the minimum energy configuration of Se_5 . The envelope structure is a closed configuration with two interior angles of 117° , two of 70° , and one of 132° . (Oligschleger reports an envelope structure with four bond angles of 100° and one of 87° .) While the envelope configuration is indeed a local minimum in the Se_5 potential energy landscape, it is much less favorable than the regular pentagon of inherent structure **A**.

Transitions between degenerate chains **B** can be accomplished with a change in torsion, as indicated by point **F** in Figure 9.6. This is also true of transitions between degenerate chains **C**, which occur through transition point **H**. The activation energy required for these isostructural transitions is much less than that required for transitions between any two non-degenerate inherent structures. Transitions among the degenerate envelope configurations **E** can be accomplished with minimal energy through transition point **G**. It is also possible to transition between closed configurations **A** and **E** without breaking any

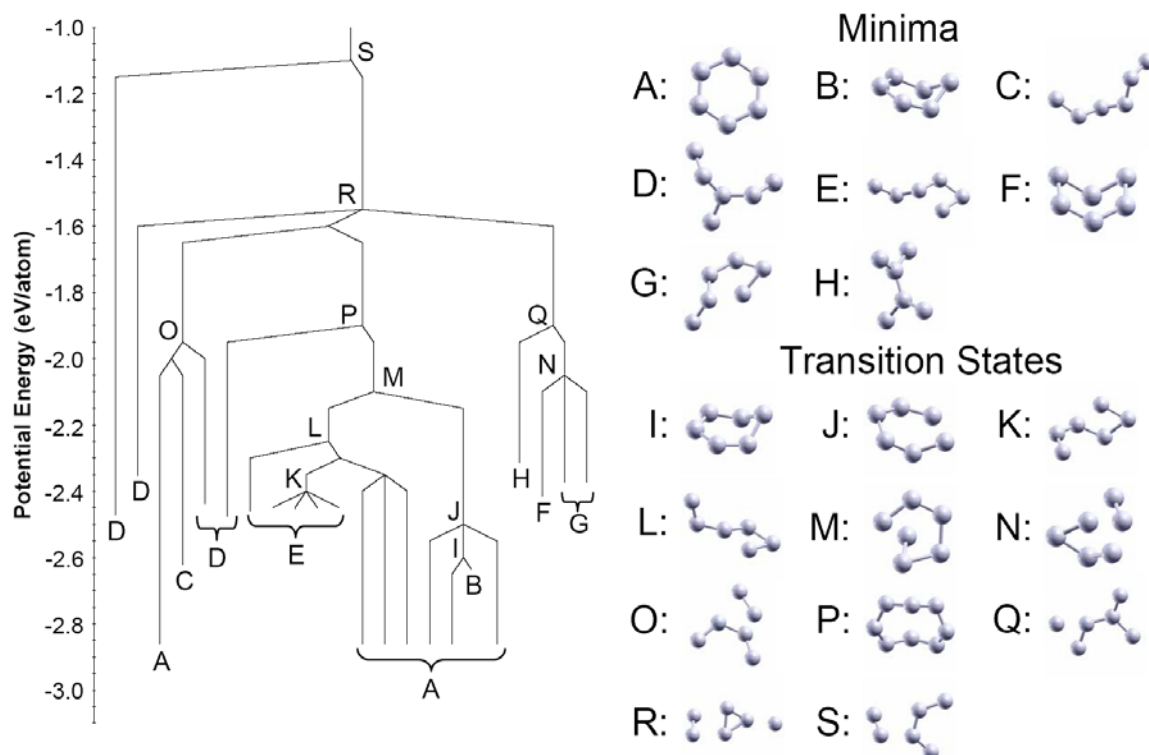


Figure 9.7. Disconnectivity graph for Se_6 and plots of the identified minimum energy structures and transition states.

bonds. All other transitions, including those between chain and ring structures and between non-degenerate chain structures, involve bond breakage. As indicated by transition points I, J, and K, this can occur along several different routes.

The five-atom selenium cluster represents a cross-over for when a closed structure becomes most favorable. While open chain configurations are most favorable for Se_3 and Se_4 , Se_5 and, as we shall see soon, Se_6 - Se_8 clusters all have a closed ring geometry as their global minimum in energy.

9.2.4 Se_6

The potential energy landscape of Se_6 , shown by the disconnectivity graph in Figure 9.7, is rich with inherent structures and transition points. The global minimum, labeled A, is a regular hexagon. This is not surprising, given the favorable bond angle of 120° . Two other closed inherent structures, B and F, also exist but are less favorable. The B geometry consists of five atoms bonded in a plane with bond angles of 112° . The sixth atom is out-of-plane and closes the ring with an interior angle of 70° . Inherent structure F is a “canoe” with two 72° , two 122° , and two 120° interior angles. The minimum energy configuration proposed by Oligschleger¹⁴ is a variation on inherent structure B, but with a second atom out-of-plane. This is not found to be a favorable inherent structure using our *ab initio* potentials.

The most favorable chain structure of Se_6 is that of point C in Figure 9.7, which incorporates all 117° bond angles. Other chain structures, such as E and G, incorporate less favorable bond angles. Inherent structures D and H both incorporate all 117° bonds, but at the cost of having one or two three-coordinated selenium atoms, respectively.

Transitions between closed geometries A and B are allowed through point I, which has only slightly higher energy than the local minimum B. It is not favorable for A or B to transition to the third closed configuration F without bond breakage, as indicated by transition points R and N, respectively. We have seen in the case of the Se_4 landscape that transitions within degenerate chain structures are much easier if the chains incorporate a 65° angle. This is also true for Se_6 , where there is little activation barrier to move from minimum E to transition point K. Transitions between A and E through point L are also

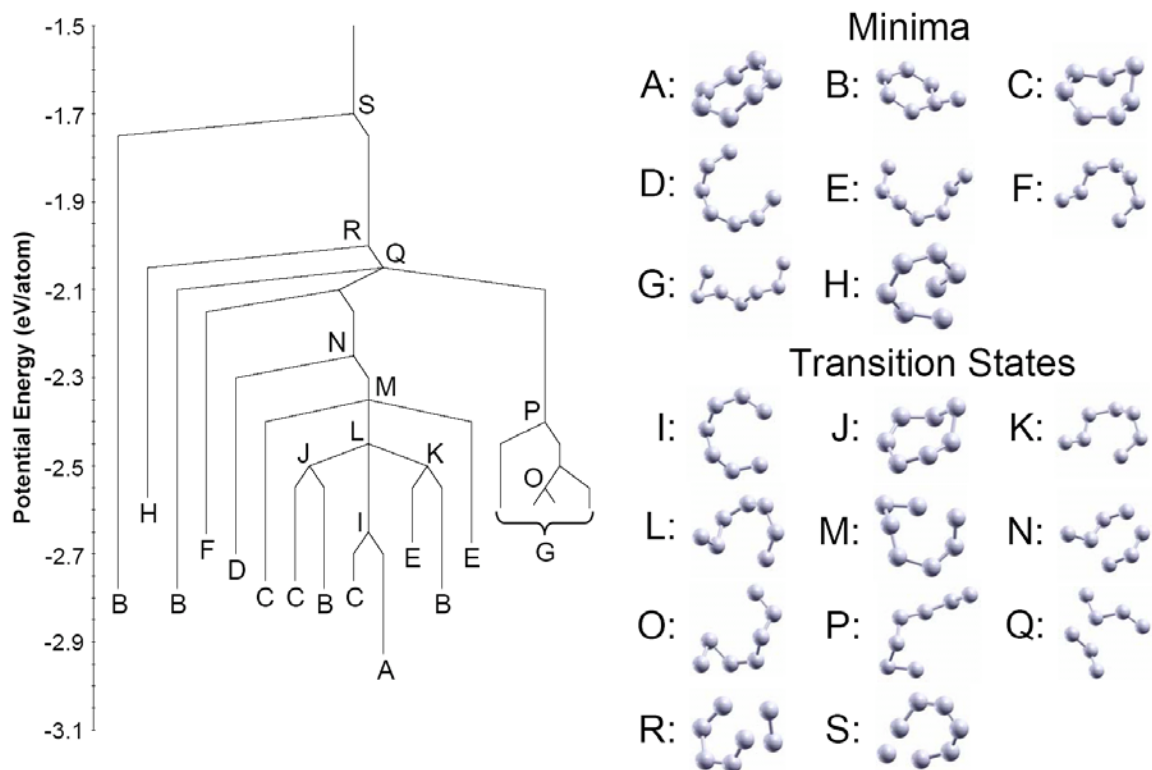


Figure 9.8. Disconnectivity graph for Se_7 and plots of the identified minimum energy structures and transition states.

possible while keeping the Se_6 cluster intact. Transitions from D to A, B, or E can be accomplished through ring structure P. Other transitions favor a fragmentation of the Se_6 cluster into smaller pieces.

9.2.5 Se_7

The global minimum of the Se_7 potential energy landscape is the ring structure indicated by point A in Figure 9.8, which incorporates bond angles of about 120° . The atoms are not in-plane with each other. The next most favorable configuration of Se_7 , labeled B, is a regular hexagon with the seventh atom bonded at 117° angles to one of the

six atoms in the hexagon, resulting in one three-coordinated atom. Inherent structure C has an only slightly higher energy and consists of six atoms bonded at 119° angles, nearly in a plane. The seventh atom closes the ring from out-of-plane, incorporating a bond angle of 65° . The remaining inherent structures are variations on the familiar chain motif. As usual, the energy of the chains increases as less favorable angles are incorporated into the structure.

Transitions between ring structures A and C are possible with chain I as an intermediate state. Transitions between inherent structures B and C are possible via the ring transition state J. Isostructural transitions among the degenerate G chains can occur with minimal energy through point O or through the less favorable transition state P. Other transition states include the chain structures L and M and the higher-energy fragmented states Q, R, and S.

The semi-empirical modeling of Oligschleger predicts a “chair” configuration as the most stable configuration of Se_7 . This is similar to our inherent structure C in Figure 9.8, but with two additional atoms out-of-plane. Since inherent structure A incorporates more favorable angles, it is more likely to be the true global minimum for Se_7 .

9.3 Elemental Clusters (S_8 , Se_8 , and Te_8)

Disconnectivity graphs for S_8 , Se_8 , and Te_8 clusters are found in Figures 9.9-9.11. The global energy minimum in all three cases is the familiar “crown” structure, which is experimentally well-known for both S_8 ^{?,57,58} and Se_8 .^{14,241} While there is no experimental data on the Te_8 cluster, it is not surprising that it should also adopt the crown configuration

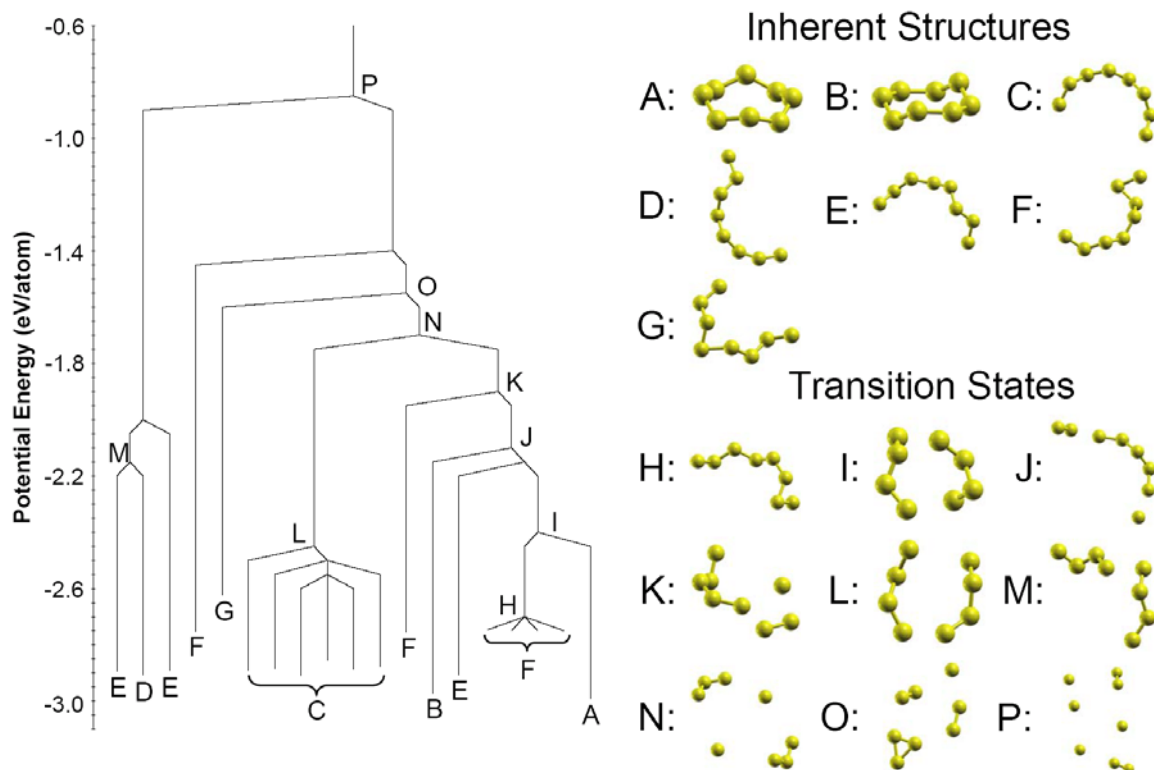


Figure 9.9. Disconnectivity graph for S_8 and plots of the identified inherent structures and transition states.

as its lowest energy state. In all three cases, ring structures have consistently lower energy than chain configurations. Ring structures are especially stable in the Se_8 cluster, where there are several variations on the crown motif. Overall, the seven ring configurations of Se_8 (labeled A-G in Figure 9.10) are shown to be significantly more favorable than Se_8 chains (H-J). Transitions among many of the Se_8 rings are possible through several ring transition states (K-N), and the chain transition state O allows for transition among all seven distinct types of Se_8 rings. Transitions between chains and rings and between the various types of chains are possible through fragmented states (P-R). As shown in Table XV, Se_8 has a lower potential energy per atom than any of the Se_3 - Se_7 clusters, indicating that Se_8 is

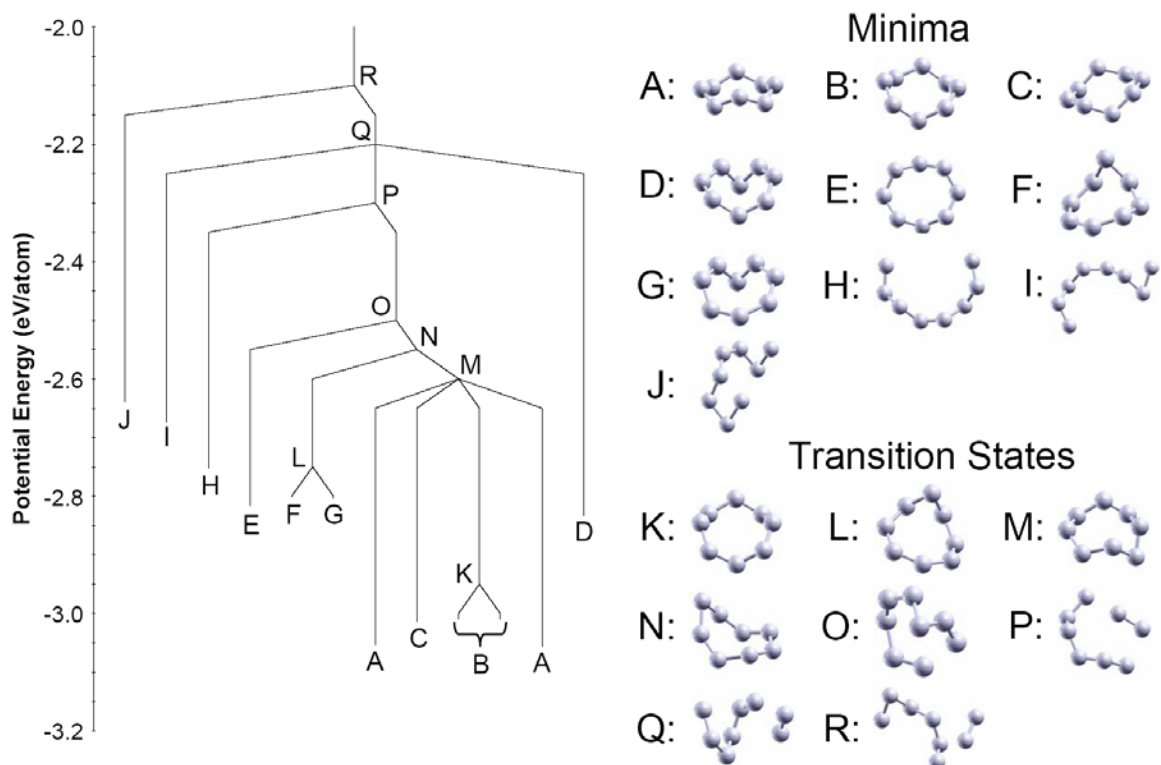


Figure 9.10. Disconnectivity graph for Se_8 and plots of the identified inherent structures and transition states.

more favorable overall than the smaller clusters.

There are fewer distinct rings in both S_8 and Te_8 than in Se_8 , with the sulfur cluster having only two available ring formations. This is due to the S-S-S triple having a difference of about 0.8 eV between energy minima at the large bond angle ($\sim 118^\circ$) as compared to the less favorable small bond angle ($\sim 65^\circ$), while in Se-Se-Se these minima are comparable. Hence Se_8 rings can involve combinations of large and small bond angles, whereas favorable ring formations of S_8 involve only angles near the 118° minimum. Moreover, the large angle minimum for Se-Se-Se is significantly broader than that of S-S-S, allowing for greater bond angle flexibility in the Se_8 structures. Therefore, a much greater variety of ring structures

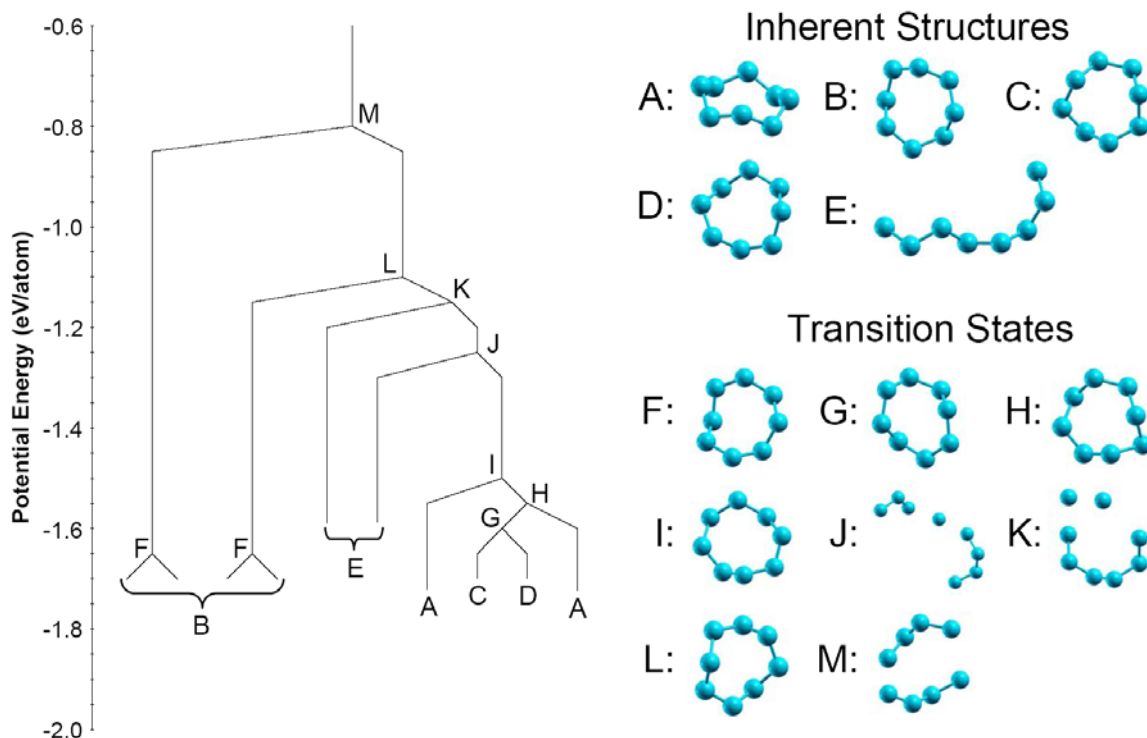


Figure 9.11. Disconnectivity graph for Te_8 and plots of the identified inherent structures and transition states.

is allowed in Se_8 as compared to S_8 .

The tellurium cluster has four rings, an intermediate number between S_8 and Se_8 . Like S_8 , Te_8 has no rings containing the small bond angle ($\sim 65^\circ$); however, in this case the explanation relates to the relative strength of the two- and three-body interaction potentials. The two-body interaction potential for Te-Te is about 0.5 eV/atom weaker than that of Se-Se and nearly 1 eV/atom weaker than that of sulfur. However, the three-body potential of Te-Te-Te is comparable to that of Se-Se-Se at the small angle minimum. For larger clusters such as Te_8 , the repulsive three-body contribution therefore dominates over the attractive two-body contributions at the 65° angle, making rings containing these small angles unfavorable. Likewise, tellurium chains with 65° angles are not present in Figure

Table XV. Lowest Energy Values of Selenium Clusters

Cluster	Minimum Potential (eV/atom)
Se ₃	−2.04
Se ₄	−2.36
Se ₅	−2.74
Se ₆	−2.86
Se ₇	−2.93
Se ₈	−3.05

9.11. The potential energies of all Te₈ inherent structures are much higher than both S₈ and Se₈ owing to tellurium’s weaker two-body binding energy.

The lowest-energy chain configurations in both S₈ and Te₈ are much closer in energy to their corresponding ring states than for Se₈. While S₈ and Se₈ each have one chain transition state, the transition states in Te₈ are all rings or fragments. The chain transition state H for S₈ in Figure 9.9 includes a 65° angle and allows for transitions among the various degenerate states of chain C. All of the transition points between non-degenerate states of S₈ involve bond breakage, unlike Se₈ and Te₈ where several ring transition states are possible.

9.4 Se_nTe_{8−n} Clusters

We plot disconnectivity graphs for Se₆Te₂, Se₄Te₄, and Se₂Te₆ in Figures 9.12-9.14, respectively. As with the elemental clusters, the “crown” structure is the global minimum in energy for Se_nTe_{8−n}. However, we may note one key difference between the Se₂Te₆ crown and the crown structures of Se₄Te₄ and Se₆Te₂. Whereas the selenium and tellurium atoms are segregated from each other in the Se₄Te₄ and Se₆Te₂ crowns, the two selenium atoms

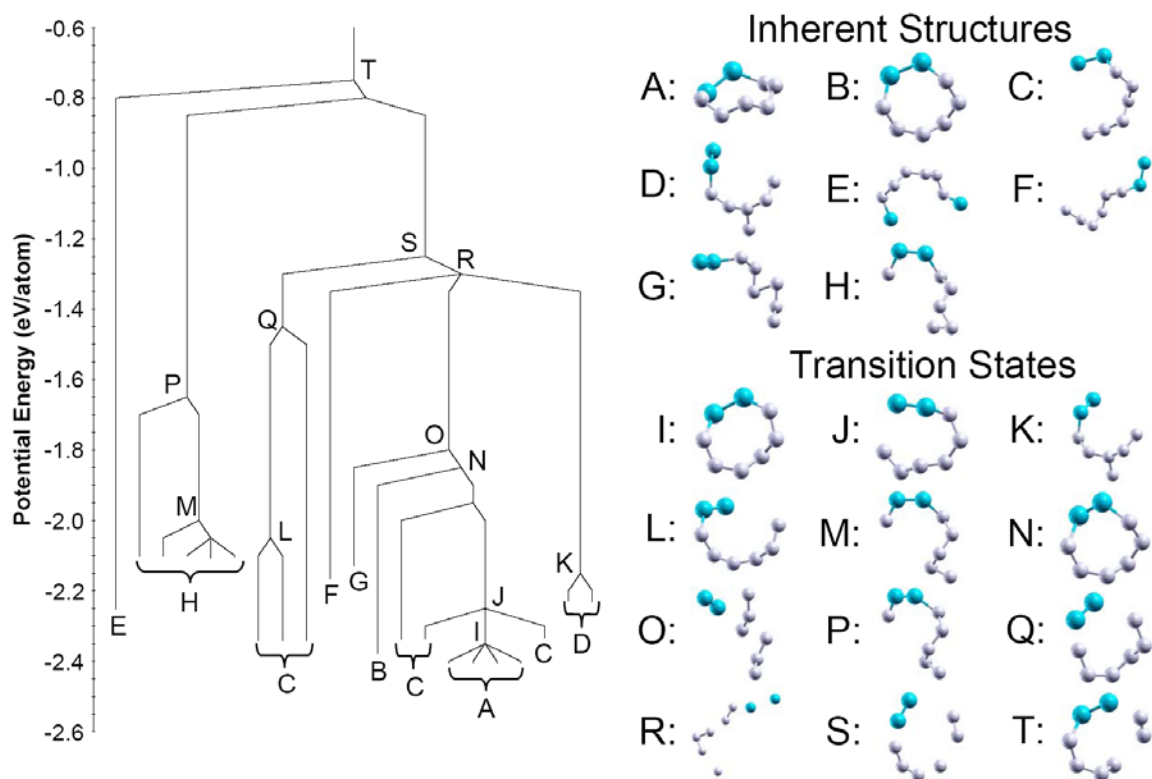


Figure 9.12. Disconnectivity graph for Se_6Te_2 and plots of the identified inherent structures and transition states.

in Se_2Te_6 crown are separated by a tellurium atom. In fact, this trend is continued for almost all of the inherent structures in the $\text{Se}_n\text{Te}_{8-n}$ clusters. While heteropolar bonding is kept to a minimum in Se_4Te_4 and Se_6Te_2 , it tends to be maximized in Se_2Te_6 .

This very interesting result is similar to a result obtained in our Monte Carlo simulations of bulk $\text{Se}_x\text{Te}_{1-x}$ glass structure, where we found that heterogenous $\text{Se}_x\text{Te}_{1-x}$ glasses are almost entirely phase separated at the chain level for $x > 0.2$. However, at low values of x selenium was found to be highly soluble in the tellurium matrix. The usual preference for homopolar bonding in selenium-tellurium mixtures is apparent from the two-body interaction potentials, since the strength of the heteropolar Se-Te bond is weaker than

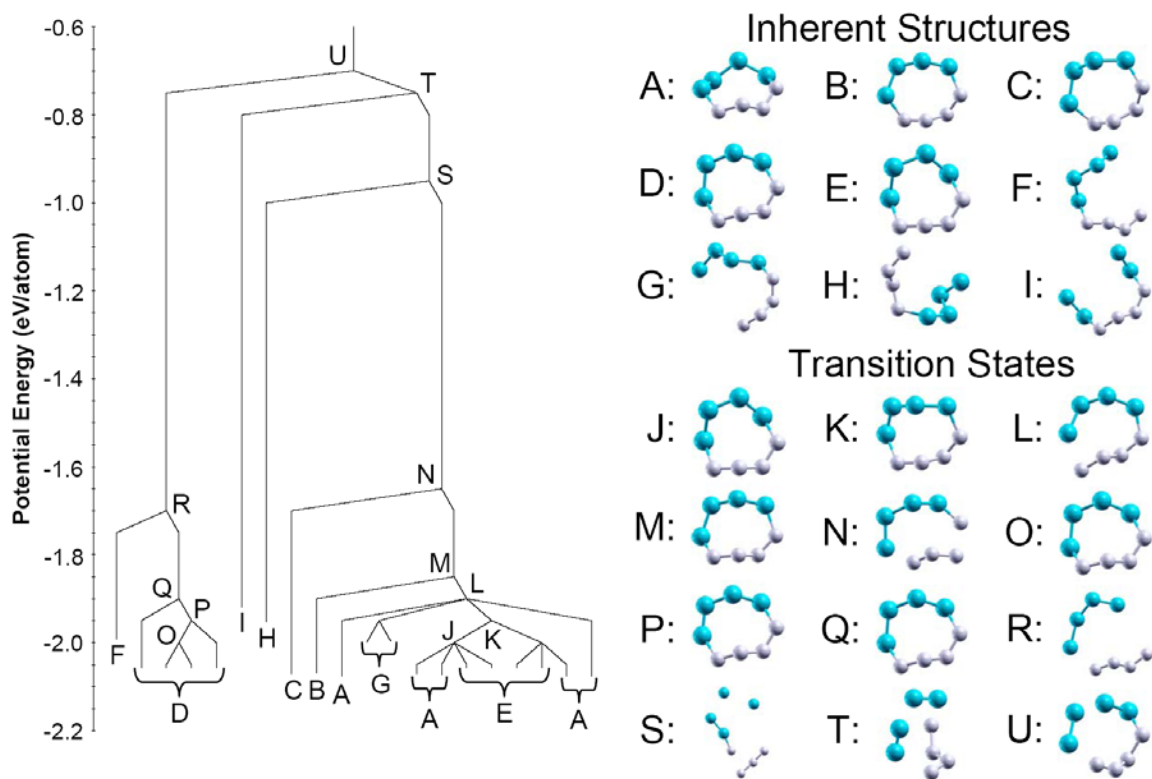


Figure 9.13. Disconnectivity graph for Se_4Te_4 and plots of the identified inherent structures and transition states.

the average of the homopolar Se-Se and Te-Te bonds. However, this does not explain the preference for heteropolar bonding at low concentration of selenium.

This result in $\text{Se}_x\text{Te}_{1-x}$ glasses may be elucidated by considering the inherent structures of the Se_2Te_6 cluster in Figure 9.14. Since it is impossible to have an Se-Se-Se group in Se_2Te_6 , the available three-body combinations of atoms involving selenium are Se-Se-Te, Se-Te-Te, Se-Te-Se, and Te-Se-Te. Of these, the three-body repulsion at 118° of Se-Se-Te is the strongest, more than compensating for the stronger binding energy of the Se-Se pair. As a result, inherent structures in Se_2Te_6 favor heteropolar Se-Te-Se and Te-Se-Te bonding. A similar argument can be made to explain the solubility of a small

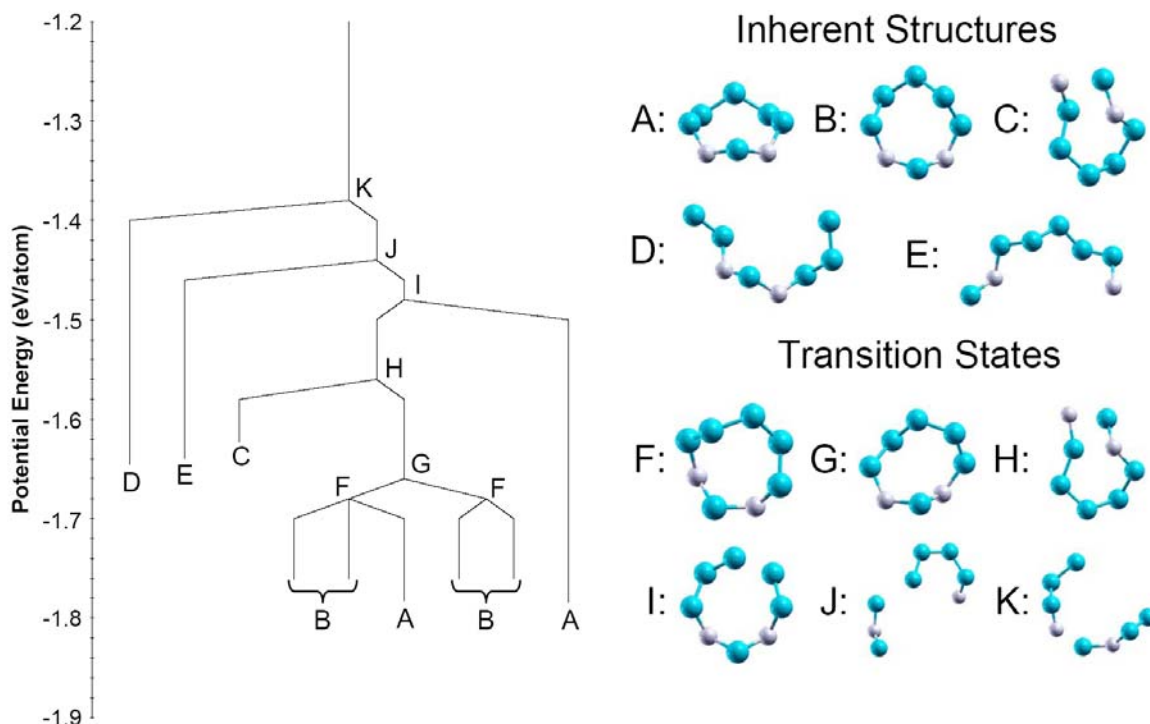


Figure 9.14. Disconnectivity graph for Se_2Te_6 and plots of the identified inherent structures and transition states.

concentration of selenium atoms in a predominantly telluride glass.

Another interesting result is that the Se_4Te_4 cluster has significantly more ring formations than both Se_2Te_6 and Se_6Te_2 . Since the selenium and tellurium atoms in the Se_4Te_4 rings are completely segregated, they all contain Se-Se-Se and Te-Te-Te triples, which have a higher degree of bond flexibility around the large angle ($\sim 118^\circ$) minimum than the heterogeneous Se-Te-Se, Te-Se-Te, Se-Se-Te, and Se-Te-Te triples. As a result, Se_4Te_4 is able to form a greater number of distinct ring configurations. However, none of these rings include any small angle ($\sim 65^\circ$) bonding. This is due to the same reason that small angle bonds are absent in the elemental Te_8 cluster: the repulsion due to three-body interaction at 65° outweighs the attractive potentials of the two-body interaction.

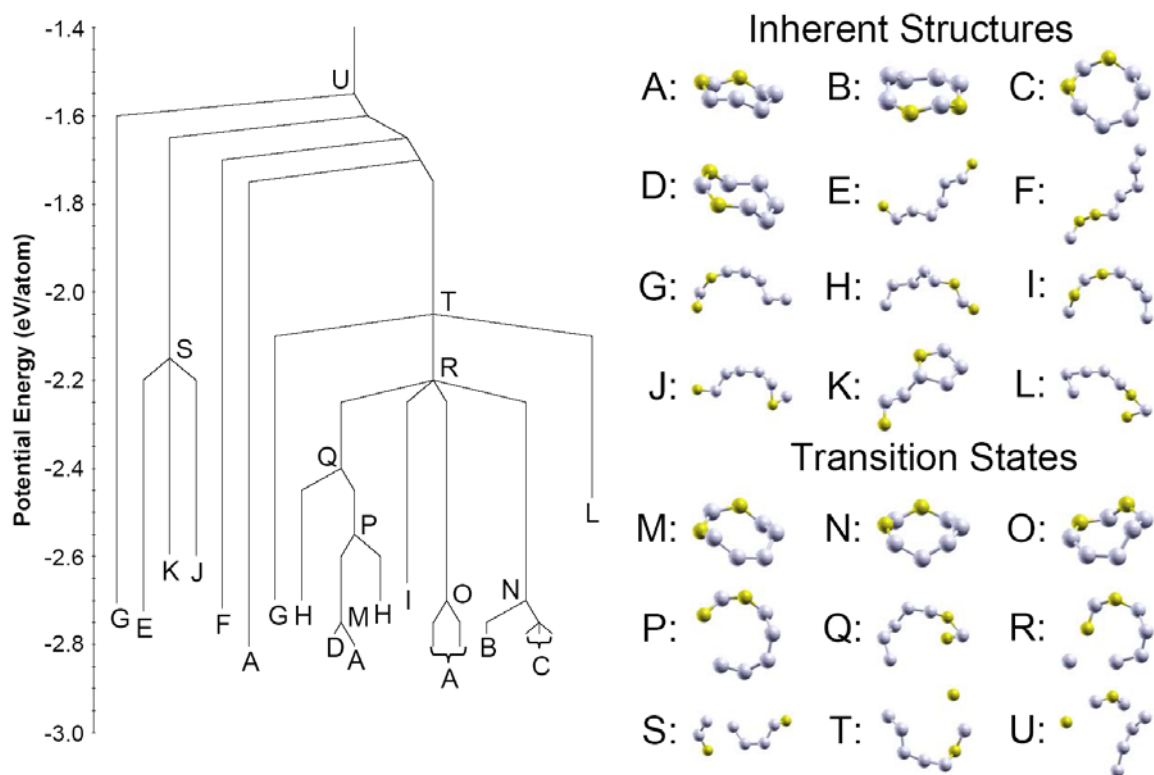


Figure 9.15. Disconnectivity graph for Se_6S_2 and plots of the identified inherent structures and transition states.

9.5 $\text{Se}_n\text{S}_{8-n}$ Clusters

Disconnectivity graphs for Se_6S_2 , Se_4S_4 , and Se_2S_6 clusters are shown in Figures 9.15-9.17. As with the other chalcogen clusters, the $\text{Se}_n\text{S}_{8-n}$ clusters all have the “crown” configuration as the global minimum in energy. However, unlike the case of $\text{Se}_n\text{Te}_{8-n}$, the $\text{Se}_n\text{S}_{8-n}$ rings are able to include small angle ($\sim 65^\circ$) bonding since the two- plus three-body interactions at 65° are not as unfavorable for the sulfur-selenium triples as for the selenium-tellurium triples.

The $\text{Se}_n\text{S}_{8-n}$ clusters show an interesting trend with respect to segregation. Whereas the sulfur and selenium atoms in the inherent structures of Se_4S_4 are mostly segregated,

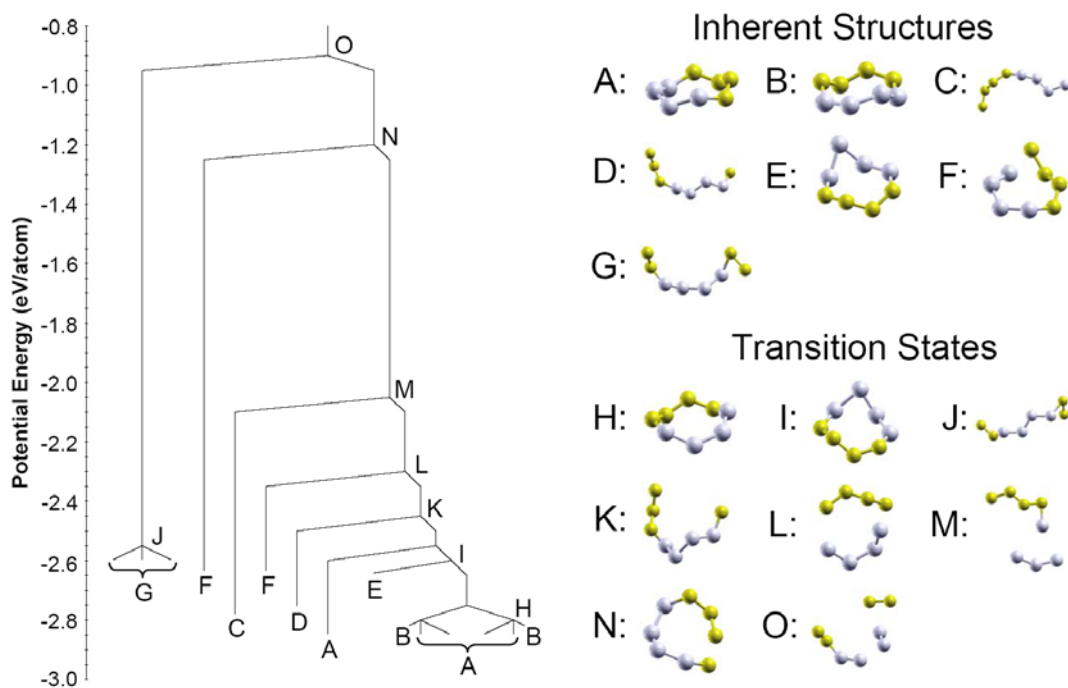


Figure 9.16. Disconnectivity graph for Se_4S_4 and plots of the identified inherent structures and transition states.

both Se_6S_2 and Se_2S_6 clusters favor heteropolar bonding. The segregation in Se_4S_4 can be explained in terms of the two-body interactions. Since the S-Se bond strength is less than the average of the S-S and Se-Se bond strengths, homopolar bonding is generally preferable. However, three-body effects cause heteropolar bonding to be favorable in the Se_6S_2 and Se_2S_6 clusters. Since the three-body potentials at the 118° minimum are greater for S-S-Se and Se-Se-S than for S-Se-S and Se-S-Se, heteropolar bonding becomes favorable. This does not affect the preference for segregation in Se_4S_4 since both the S-S-S and Se-Se-Se triples have a low three-body potential around 118° . These results for $\text{Se}_n\text{S}_{8-n}$ clusters help explain the preference for homopolar bonding in $\text{Se}_x\text{S}_{1-x}$ glasses with $x \approx 0.5$, while heteropolar bonding becomes preferable for both high and low x .

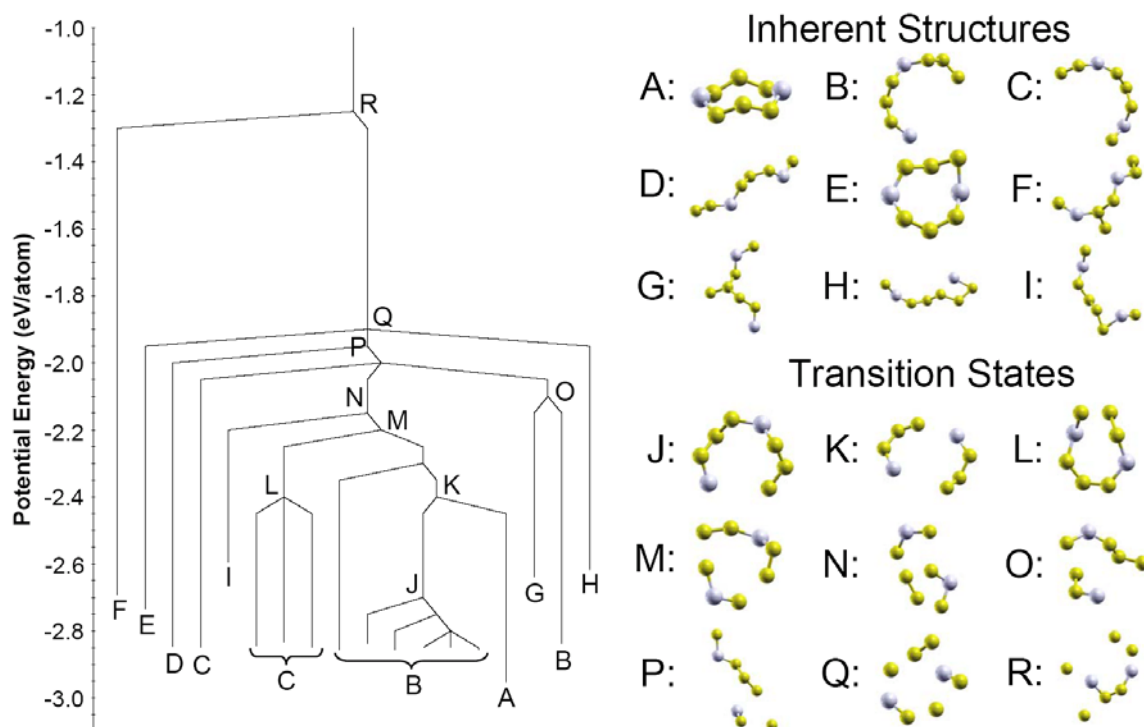


Figure 9.17. Disconnectivity graph for Se_2S_6 and plots of the identified inherent structures and transition states.

The preference for S-Se-S and Se-S-Se triples in Se_6S_2 also contributes to a greater variety of ring structures allowable in this cluster since both the S-Se-S and Se-S-Se three-body potentials are fairly broad around at 118° minimum. This is not the case in Se_2S_6 due to the narrowness of the S-S-S three-body minimum. Furthermore, there are no ring transition states present in Se_2S_6 .

9.6 Conclusions

We have presented a thorough description of the potential energy landscapes of small chalcogen clusters using *ab initio* potentials and our eigenvector-following approach for

locating transition states. Whereas chain structures are found to be most favorable for Se_3 and Se_4 clusters, ring structures are dominant in Se_5 - Se_8 . The “crown” structure serves as the global energy minimum for all of the eight-body chalcogen clusters under investigation. Ring structures are generally more favorable than chains, but the number of favorable rings depends on the nature of the three-body interactions. Segregation in heterogeneous clusters is due to two-body effects but can be overcome by appropriate three-body interactions. Isostructural transitions between degenerate states can often be accomplished with little activation energy. Transitions between highly dissimilar inherent structures can involve the breaking and reforming of one or more bonds.

Inherent structures in these chalcogen clusters can provide insights into the structure of bulk chalcogen glasses. In particular, the solubility of selenium in a heterogeneous $\text{Se}_x\text{Te}_{1-x}$ glass with small x can be explained by analogy to the $\text{Se}_n\text{Te}_{8-n}$ clusters, where heteropolar bonding is preferred for small n . In this case, Se-Te-Se and Te-Se-Te triples are preferred over Se-Se-Te due to the more favorable three-body interactions around bond angles of 118° . Analogous results for $\text{Se}_n\text{S}_{8-n}$ clusters explain the preference for homopolar bonding in $\text{Se}_x\text{S}_{1-x}$ glasses with $x \approx 0.5$, while heteropolar bonding becomes preferable for both high and low x .

Chapter 10

Mapping of Enthalpy Landscapes

Recently, there have been many studies involving potential energy landscapes of molecular clusters,^{222–225} biomolecules,²²⁵ supercooled liquids,^{167,177} and glassy systems.^{225–227} Potential energy landscapes do not allow for changes in the volume of a system and are thus inadequate for understanding structural relaxation in inorganic glasses. A recent study by Middleton and Wales²²⁷ introduced the concept of an enthalpy landscape and applied it to a model glass system under isobaric conditions. Exploration of an enthalpy landscape allows for changes in both particle positions and the total volume of the system. In order to separate the thermal and configurational components of energy, the enthalpy landscape is computed at absolute zero. This zero temperature landscape corresponds to an underlying surface that is sampled by a system at finite temperature in an isobaric ensemble.

In this chapter, we derive a new eigenvector-following technique for locating minima and transition points in an enthalpy landscape. Our derivation is based on our previ-

ous study of potential energy landscapes (Chapter 8), in which we used steepest descents to find minima and an eigenvector-following method to locate first-order transition points. However, for bulk systems with periodic boundary conditions, the method of steepest descent has convergence issues due to the tortuosity of the enthalpy landscape. To this end, we present a recursive algorithm for mapping enthalpy landscapes that incorporates eigenvector-following methods for locating both minima and transition points.

Our new eigenvector-following technique includes two steps at each iteration in order to independently vary system volume and relative atomic positions. The justification for this approach is discussed in Sections 10.1-10.3, and the split-step technique itself is presented in Sections 10.4-10.5. A recursive algorithm for mapping enthalpy landscapes is provided in Section 10.6. Using this algorithm, we partially map the enthalpy landscape of a bulk selenium system and compute a preliminary volume-temperature diagram.

10.1 The Difficulty of Enthalpy Landscapes

The zero temperature enthalpy landscape of an N -particle system is

$$\mathcal{H} = E(x_1, x_2, \dots, x_{3N}, V) + PV, \quad (10.1)$$

where the potential (i.e., configurational) energy E is a function of $3N$ position coordinates, $x_1, x_2, \dots, x_{3N}$, and the volume V of the simulation cell. The pressure P of the system is constant. The enthalpy landscape therefore has a dimensionality of $3N + 1$, minus any constraints.

If the enthalpy of the system with initial positions x_i^0 , where $i = 1, 2, \dots, 3N$, and

initial volume V^0 is given by $\mathcal{H}(x_i^0, V^0)$, then we may approximate the enthalpy at a new position $x_i = x_i^0 + h_i$ and new volume $V = V^0 + h_V$ using the Taylor series expansion,

$$\begin{aligned}
\mathcal{H}(x_i, V) \approx & \mathcal{H}(x_i^0, V^0) + \sum_{i=1}^{3N} \left. \frac{\partial \mathcal{H}}{\partial x_i} \right|_{x_i=x_i^0, V=V^0} h_i + \left. \frac{\partial \mathcal{H}}{\partial V} \right|_{x_i=x_i^0, V=V^0} h_V \\
& + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \left. \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \right|_{x_{i,j}=x_{i,j}^0, V=V^0} h_j + \frac{1}{2} \left. \frac{\partial^2 \mathcal{H}}{\partial V^2} \right|_{x_i=x_i^0, V=V^0} h_V^2 \\
& + \frac{1}{2} \sum_{i=1}^{3N} h_i \left. \frac{\partial^2 \mathcal{H}}{\partial x_i \partial V} \right|_{x_i=x_i^0, V=V^0} h_V \\
& + \frac{1}{2} \sum_{i=1}^{3N} h_V \left. \frac{\partial^2 \mathcal{H}}{\partial V \partial x_i} \right|_{x_i=x_i^0, V=V^0} h_i.
\end{aligned} \tag{10.2}$$

For computational convenience, it is desirable to give all $3N + 1$ coordinates the dimensions of length. If we assume a cubic volume of $V = L^3$, the enthalpy can be rewritten as

$$\mathcal{H} = E(x_1, x_2, \dots, x_{3N}, L) + PL^3, \tag{10.3}$$

such that

$$\begin{aligned}
\mathcal{H}(x_i, L) \approx & \mathcal{H}(x_i^0, L^0) + \sum_{i=1}^{3N} \left. \frac{\partial \mathcal{H}}{\partial x_i} \right|_{x_i=x_i^0, L=L^0} h_i + \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{x_i=x_i^0, L=L^0} h_L \\
& + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \left. \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \right|_{x_{i,j}=x_{i,j}^0, L=L^0} h_j + \frac{1}{2} \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{x_i=x_i^0, L=L^0} h_L^2 \\
& + \frac{1}{2} \sum_{i=1}^{3N} h_i \left. \frac{\partial^2 \mathcal{H}}{\partial x_i \partial L} \right|_{x_i=x_i^0, L=L^0} h_L \\
& + \frac{1}{2} \sum_{i=1}^{3N} h_L \left. \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \right|_{x_i=x_i^0, L=L^0} h_i.
\end{aligned} \tag{10.4}$$

This can be written in matrix notation as

$$\mathcal{H}(\mathbf{q}) \approx \mathcal{H}(\mathbf{q}^0) + \mathbf{g}^\top \mathbf{h} + \frac{1}{2} \mathbf{h}^\top \mathbf{H} \mathbf{h}, \quad (10.5)$$

where the position vectors are given by

$$\mathbf{q} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{3N} \\ L \end{pmatrix}; \quad \mathbf{q}^0 = \begin{pmatrix} x_1^0 \\ x_2^0 \\ \vdots \\ x_{3N}^0 \\ L^0 \end{pmatrix} \quad (10.6)$$

and the displacement vector $\mathbf{h} = \mathbf{q} - \mathbf{q}^0$ is

$$\mathbf{h} = \begin{pmatrix} h_1 \\ h_2 \\ \vdots \\ h_{3N} \\ h_L \end{pmatrix}. \quad (10.7)$$

The gradient vector $\mathbf{g}$ and the $(3N + 1) \times (3N + 1)$ Hessian matrix $\mathbf{H}$, evaluated at $\mathbf{q} = \mathbf{q}^0$,

are given by

$$\mathbf{g} = \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial x_1} \\ \frac{\partial \mathcal{H}}{\partial x_2} \\ \vdots \\ \frac{\partial \mathcal{H}}{\partial x_{3N}} \\ \frac{\partial \mathcal{H}}{\partial L} \end{pmatrix}_{\mathbf{q}=\mathbf{q}^0} \quad (10.8)$$

and

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 \mathcal{H}}{\partial x_1^2} & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial L} \\ \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial x_1} & \frac{\partial^2 \mathcal{H}}{\partial x_2^2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial L} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \frac{\partial^2 \mathcal{H}}{\partial x_{3N} \partial x_1} & \frac{\partial^2 \mathcal{H}}{\partial x_{3N} \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_{3N}^2} & \frac{\partial^2 \mathcal{H}}{\partial x_{3N} \partial L} \\ \frac{\partial^2 \mathcal{H}}{\partial L \partial x_1} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial L^2} \end{pmatrix}_{\mathbf{q}=\mathbf{q}^0}, \quad (10.9)$$

respectively.

In our previous derivation of an eigenvector-following technique for potential energy landscapes (Chapter 8), the Hessian matrix $\mathbf{H}$ contained second derivatives with respect to position coordinates x_i only. Since the position coordinates are independent of each other,

$$\frac{\partial^2 E}{\partial x_i \partial x_j} = \frac{\partial^2 E}{\partial x_j \partial x_i}, \quad (10.10)$$

so the Hessian matrix is symmetric. In the case of an enthalpy landscape, the Hessian matrix has one additional row and column including derivatives with respect to the simulation cell length L . The chief difficulty in extending our potential energy approach to enthalpy landscapes is that the position and length coordinates are not truly independent of each

other. When implementing a change in length for a bulk system with periodic boundary conditions, it is standard to scale the atomic positions according to

$$\frac{\partial x_i}{\partial L} = \frac{x_i}{L}. \quad (10.11)$$

Therefore,

$$\frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} = \sum_{j=1}^{3N} \frac{\partial x_j}{\partial L} \frac{\partial}{\partial x_j} \frac{\partial \mathcal{H}}{\partial x_i} = \sum_{j=1}^{3N} \frac{x_j}{L} \frac{\partial^2 \mathcal{H}}{\partial x_j \partial x_i}, \quad (10.12)$$

and

$$\frac{\partial^2 \mathcal{H}}{\partial x_i \partial L} = \frac{\partial}{\partial x_i} \sum_{j=1}^{3N} \frac{\partial x_j}{\partial L} \frac{\partial \mathcal{H}}{\partial x_j} = \sum_{j=1}^{3N} \frac{x_j}{L} \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} + \frac{1}{L} \frac{\partial \mathcal{H}}{\partial x_i}. \quad (10.13)$$

Thus,

$$\frac{\partial^2 \mathcal{H}}{\partial x_i \partial L} = \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} + \frac{1}{L} \frac{\partial \mathcal{H}}{\partial x_i}, \quad (10.14)$$

and the Hessian matrix $\mathbf{H}$ for an enthalpy landscape is not symmetric. This poses a problem in computing the eigenvalues and eigenvectors of $\mathbf{H}$, since most eigenvector solvers assume a symmetric matrix; those that allow for asymmetric matrices are much less efficient than symmetric eigenvector solvers. In addition, an asymmetric matrix can lead to complex eigenvalues.

Fortunately, we can take advantage of the relationship in Equation (10.14) to

symmetrize the Hessian. Substituting Equation (10.14) into (10.4), we obtain

$$\begin{aligned}
\mathcal{H}(x_i, L) \approx & \mathcal{H}(x_i^0, L^0) + \sum_{i=1}^{3N} \frac{\partial \mathcal{H}}{\partial x_i} \Big|_{x_i=x_i^0, L=L^0} h_i + \frac{\partial \mathcal{H}}{\partial L} \Big|_{x_i=x_i^0, L=L^0} h_L \\
& + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \Big|_{x_{i,j}=x_{i,j}^0, L=L^0} h_j + \frac{1}{2} \frac{\partial^2 \mathcal{H}}{\partial L^2} \Big|_{x_i=x_i^0, L=L^0} h_L^2 \\
& + \frac{1}{2} \sum_{i=1}^{3N} h_i \left(\frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} + \frac{1}{L} \frac{\partial \mathcal{H}}{\partial x_i} \right) \Big|_{x_i=x_i^0, L=L^0} h_L \\
& + \frac{1}{2} \sum_{i=1}^{3N} h_L \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \Big|_{x_i=x_i^0, L=L^0} h_i,
\end{aligned} \tag{10.15}$$

which simplifies to

$$\begin{aligned}
\mathcal{H}(x_i, L) \approx & \mathcal{H}(x_i^0, L^0) + \sum_{i=1}^{3N} \left(1 + \frac{h_L}{L} \right) \frac{\partial \mathcal{H}}{\partial x_i} \Big|_{x_i=x_i^0, L=L^0} h_i + \frac{\partial \mathcal{H}}{\partial L} \Big|_{x_i=x_i^0, L=L^0} h_L \\
& + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \Big|_{x_{i,j}=x_{i,j}^0, L=L^0} h_j + \frac{1}{2} \frac{\partial^2 \mathcal{H}}{\partial L^2} \Big|_{x_i=x_i^0, L=L^0} h_L^2 \\
& + \sum_{i=1}^{3N} h_L \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \Big|_{x_i=x_i^0, L=L^0} h_i.
\end{aligned} \tag{10.16}$$

This can be rewritten in matrix notation as

$$\mathcal{H}(\mathbf{q}) \approx \mathcal{H}(\mathbf{q}^0) + \left(1 + \frac{h_L}{L} \right) \mathbf{g}^\top \mathbf{h} + \frac{1}{2} \mathbf{h}^\top \mathbf{H}' \mathbf{h}, \tag{10.17}$$

where $\mathbf{H}'$ is the symmetrized Hessian

$$\mathbf{H}' = \begin{pmatrix} \frac{\partial^2 \mathcal{H}}{\partial x_1^2} & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_1} \\ \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_2} & \frac{\partial^2 \mathcal{H}}{\partial x_2^2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_2} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \frac{\partial^2 \mathcal{H}}{\partial x_1 \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial x_2 \partial x_{3N}} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial x_{3N}^2} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_{3N}} \\ \frac{\partial^2 \mathcal{H}}{\partial L \partial x_1} & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_2} & \cdots & \frac{\partial^2 \mathcal{H}}{\partial L \partial x_{3N}} & \frac{\partial^2 \mathcal{H}}{\partial L^2} \end{pmatrix}_{\mathbf{q}=\mathbf{q}^0} \quad (10.18)$$

In order to choose appropriate steps in the x_i and L dimensions, we define the Lagrange function

$$\begin{aligned} \mathcal{L} &= -\mathcal{H}(x, L) + \frac{1}{2} \sum_{i=1}^{3N} \lambda_i (h_i^2 - c_i^2) + \frac{1}{2} \lambda_L (h_L^2 - c_L^2) \\ &= -\mathcal{H}(x_i^0, L^0) - \sum_{i=1}^{3N} \left(1 + \frac{h_L}{L} \right) \frac{\partial \mathcal{H}}{\partial x_i} \Big|_{x_i=x_i^0, L=L^0} h_i - \frac{\partial \mathcal{H}}{\partial L} \Big|_{x_i=x_i^0, L=L^0} h_L \\ &\quad - \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \Big|_{x_{i,j}=x_{i,j}^0, L=L^0} h_j - \frac{1}{2} \frac{\partial^2 \mathcal{H}}{\partial L^2} \Big|_{x_i=x_i^0, L=L^0} h_L^2 \\ &\quad - \sum_{i=1}^{3N} h_L \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \Big|_{x_i=x_i^0, L=L^0} h_i + \frac{1}{2} \sum_{i=1}^{3N} \lambda_i (h_i^2 - c_i^2) + \frac{1}{2} \lambda_L (h_L^2 - c_L^2), \end{aligned} \quad (10.20)$$

where $c_{i,L}$ are the desired step sizes in the various directions and $\lambda_{i,L}$ are Lagrange multipliers. Taking the derivative of $\mathcal{L}$ with respect to an arbitrary step h_k and setting it equal

to zero, we obtain

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial h_k} = 0 = & - \sum_{i=1}^{3N} \left(1 + \frac{h_L}{L}\right) \frac{\partial \mathcal{H}}{\partial x_i} \Big|_{x_i=x_i^0, L=L^0} \delta_{ik} - \sum_{i=1}^{3N} \frac{h_i}{L} \frac{\partial \mathcal{H}}{\partial x_i} \Big|_{x_i=x_i^0, L=L^0} \delta_{kL} \\
& - \frac{\partial \mathcal{H}}{\partial L} \Big|_{x_i=x_i^0, L=L^0} \delta_{kL} - \sum_{i=1}^{3N} \sum_{j=1}^{3N} h_i \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} \Big|_{x_i, j=x_i^0, L=L^0} \delta_{jk} \\
& - \frac{\partial^2 \mathcal{H}}{\partial L^2} \Big|_{x_i=x_i^0, L=L^0} h_L \delta_{kL} - \sum_{i=1}^{3N} h_L \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \Big|_{x_i=x_i^0, L=L^0} \delta_{ik} \\
& - \sum_{i=1}^{3N} h_i \frac{\partial^2 \mathcal{H}}{\partial L \partial x_i} \Big|_{x_i=x_i^0, L=L^0} \delta_{kL} + \sum_{i=1}^{3N} \lambda_i h_i \delta_{ik} + \lambda_L h_L \delta_{kL}, \tag{10.21}
\end{aligned}$$

which can be simplified as

$$\begin{aligned}
0 = & - \sum_{i=1}^{3N} \left(1 + \frac{h_L}{L}\right) g_i \delta_{ik} - \sum_{i=1}^{3N} \frac{h_i}{L} g_i \delta_{kL} - g_L \delta_{kL} \\
& - \sum_{i=1}^{3N+1} \sum_{j=1}^{3N+1} h_i H'_{ij} \delta_{jk} + \sum_{i=1}^{3N+1} \lambda_i h_i \delta_{ik}; \tag{10.22}
\end{aligned}$$

$$0 = -g_k - \frac{h_L}{L} \sum_{i=1}^{3N} g_i \delta_{ik} - \frac{\delta_{kL}}{L} \sum_{i=1}^{3N} g_i h_i - \sum_{i=1}^{3N+1} H'_{ik} h_i + \lambda_k h_k. \tag{10.23}$$

Unfortunately, the solution to Equation (10.23) is difficult to obtain since the equations for h_i and h_L are coupled. This is actually a specific example of a more general optimization problem where the coordinates do not have a simple relationship but rather are related via partial derivatives.

10.2 A General Statement of the Problem

Suppose we want to minimize the function $f(a, b)$, where the coordinates a and b have no simple holonomic constraint, $\alpha(a, b) = 0$, but are related through the partial

derivatives:

$$\frac{\partial a}{\partial b} = c(a, b); \quad \frac{\partial b}{\partial a} = 0. \quad (10.24)$$

One solution of this problem involves decoupling of the a and b coordinates, which can be accomplished by introducing a new $\bar{a} = p(a, b)$ coordinate, where $\bar{a}$ satisfies

$$\frac{\partial \bar{a}}{\partial b} = 0. \quad (10.25)$$

The problem then becomes determination of the restrictions on $p(a, b)$ such that Equation (10.25) is satisfied.

The total differential of $\bar{a}$ is

$$d\bar{a} = \left. \frac{\partial \bar{a}}{\partial b} \right|_a db + \left. \frac{\partial \bar{a}}{\partial a} \right|_b da, \quad (10.26)$$

such that

$$\frac{\partial \bar{a}}{\partial b} = \left. \frac{\partial \bar{a}}{\partial b} \right|_a + \left. \frac{\partial \bar{a}}{\partial a} \right|_b \frac{\partial a}{\partial b} = 0. \quad (10.27)$$

Hence,

$$\left. \frac{\partial \bar{a}}{\partial a} \right|_b c(a, b) = - \left. \frac{\partial \bar{a}}{\partial b} \right|_a. \quad (10.28)$$

Taking the special case where $c(a, b)$ and $p(a, b)$ are separable:

$$c(a, b) = q(a) w(b); \quad p(a, b) = r(a) s(b). \quad (10.29)$$

Therefore,

$$s(b) \left. \frac{\partial r(a)}{\partial a} \right|_b q(a) w(b) = -r(a) \left. \frac{\partial s(b)}{\partial b} \right|_a. \quad (10.30)$$

Since there is no holonomic constraint between a and b , Equation (10.30) can be split into separate equations of a and b :

$$q(a) \frac{\partial r(a)}{\partial a} = r(a); \quad (10.31)$$

$$s(b) w(b) = -\frac{\partial s(b)}{\partial b}. \quad (10.32)$$

These equations become

$$\frac{\partial \ln r(a)}{\partial a} = \frac{1}{q(a)}; \quad (10.33)$$

$$\frac{\partial \ln s(b)}{\partial b} = -w(b), \quad (10.34)$$

and yield the solutions

$$r(a) = \exp \left(\int \frac{1}{q(a)} \partial a \right); \quad (10.35)$$

$$s(b) = \exp \left(- \int w(b) \partial b \right). \quad (10.36)$$

Thus, the coordinates can be decoupled by choosing

$$\bar{a} = \exp \left(\int \frac{1}{q(a)} \partial a - \int w(b) \partial b \right). \quad (10.37)$$

10.3 Application to Enthalpy Landscapes

In our case, the function $f(a, b)$ is the enthalpy function $\mathcal{H}(x_i, L)$, where a simple holonomic relation between x_i and L is not present. To see this point, consider a bulk system of atoms. If the length of the system changes, all of the x_i coordinates scale according to Equation (10.11), but displacement of a single atom does not produce a measurable change in L . Thus, we have

$$\frac{\partial x_i}{\partial L} = x_i \cdot \frac{1}{L}; \quad \frac{\partial L}{\partial x_i} = 0. \quad (10.38)$$

From Equation (10.37), we introduce the new coordinates $\bar{x}_i$ as

$$\bar{x}_i = \exp \left(\int \frac{1}{x_i} \partial x_i - \int \frac{1}{L} \partial L \right), \quad (10.39)$$

which simplifies to

$$\bar{x}_i = C \frac{x_i}{L} = \frac{x_i}{L}, \quad (10.40)$$

where the constant of integration C is set to unity. The normalized positions $\bar{x}_i$ are independent of changes in L since

$$\frac{\partial \bar{x}_i}{\partial L} = \frac{\partial}{\partial L} (x_i L^{-1}) = \frac{x_i}{L^2} - \frac{x_i}{L^2} = 0. \quad (10.41)$$

With this notation, the enthalpy landscape can be expressed as

$$\mathcal{H} = E(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_{3N}, L) + PL^3, \quad (10.42)$$

and the Lagrange problem simplifies to

$$\mathcal{H}(\bar{\mathbf{q}}) \approx \mathcal{H}(\bar{\mathbf{q}}^0) + \bar{\mathbf{g}}^\top \bar{\mathbf{h}} + \frac{1}{2} \bar{\mathbf{h}}^\top \bar{\mathbf{H}} \bar{\mathbf{h}}, \quad (10.43)$$

where the overbars denote use of the normalized $\bar{x}_i$ coordinates. In principle, the step vector $\bar{\mathbf{h}}$ can be calculated following the same procedure as for potential energy landscapes since the $\bar{x}_i$ and L coordinates are decoupled. However, this involves computation of first and second derivatives of enthalpy with respect to the normalized $\bar{x}_i$ coordinates rather than the natural x_i coordinates. Since x_i and L have units of length, the elements, eigenvalues, and eigenvectors of the Hessian matrix would all have the same units. While in principle this is not an issue, it eases implementation since it is more computationally convenient to compute derivatives and the step vector in terms of the unnormalized coordinates x_i . This can be accomplished using a split-step eigenvector-following technique described in the next Section.

10.4 Split-Step Eigenvector-Following Technique

The split-step eigenvector-following technique consists of iteratively stepping through the enthalpy landscape toward a minimum or transition point. Each iteration involves two steps:

1. Step of the simulation box length L while maintaining constant normalized positions $\bar{x}_i$.
2. Step of the positions x_i while maintaining constant L .

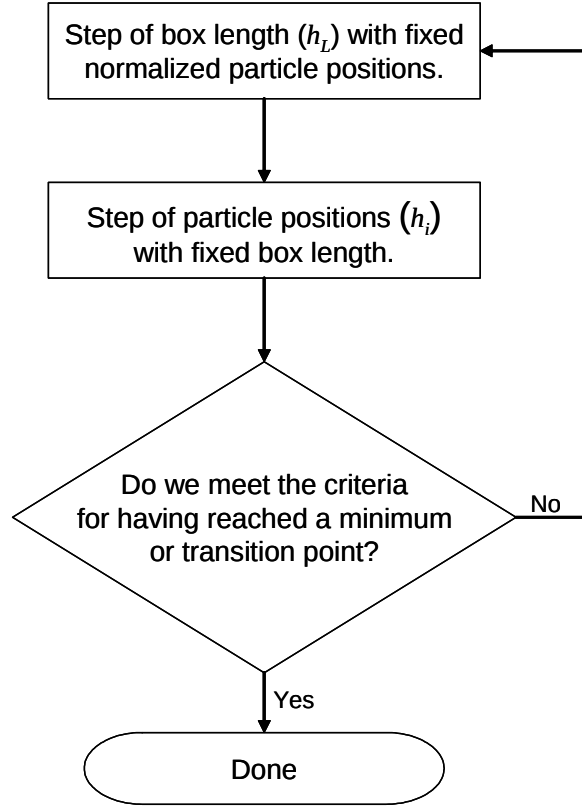


Figure 10.1. Flow chart of the split-step eigenvector-following technique for locating minima and transition points.

This procedure is shown graphically in Figure 10.1. In the first step of the iteration, the enthalpy can be written in terms of a Taylor series expansion:

$$\mathcal{H}(\bar{x}_i^0, L) \approx \mathcal{H}(\bar{x}_i^0, L^0) + \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{\bar{x}_i = \bar{x}_i^0, L = L^0} h_L + \frac{1}{2} \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{\bar{x}_i = \bar{x}_i^0, L = L^0} h_L^2. \quad (10.44)$$

We can now write a Lagrange function in one dimension:

$$\begin{aligned} \mathcal{L}_L = & -\mathcal{H}(\bar{x}_i^0, L^0) - \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{\bar{x}_i = \bar{x}_i^0, L = L^0} h_L \\ & - \frac{1}{2} \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{\bar{x}_i = \bar{x}_i^0, L = L^0} h_L^2 + \frac{1}{2} \lambda_L (h_L^2 - c_L^2). \end{aligned} \quad (10.45)$$

Taking the derivative with respect to h_L yields

$$\frac{\partial \mathcal{L}_L}{\partial h_L} = 0 = - \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{\bar{x}_i = \bar{x}_i^0, L = L^0} - \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{\bar{x}_i = \bar{x}_i^0, L = L^0} h_L + \lambda_L h_L. \quad (10.46)$$

Defining

$$F_L = \left. \frac{\partial \mathcal{H}}{\partial L} \right|_{\bar{x}_i = \bar{x}_i^0, L = L^0} = \left(\frac{\partial E}{\partial L} + 3PL^2 \right)_{\bar{x}_i = \bar{x}_i^0, L = L^0} \quad (10.47)$$

and

$$b_L = \left. \frac{\partial^2 \mathcal{H}}{\partial L^2} \right|_{\bar{x}_i = \bar{x}_i^0, L = L^0} = \left(\frac{\partial^2 E}{\partial L^2} + 6PL \right)_{\bar{x}_i = \bar{x}_i^0, L = L^0}, \quad (10.48)$$

we have

$$h_L = \frac{F_L}{\lambda_L - b_L}. \quad (10.49)$$

The change in enthalpy $\Delta \mathcal{H}_L$ for such a step h_L is

$$\Delta \mathcal{H}_L = \frac{F_L^2 \left(\lambda_L - \frac{b_L}{2} \right)}{(\lambda_L - b_L)^2}. \quad (10.50)$$

Hence, the sign of the enthalpy change depends on both b_L and the choice of Lagrange multiplier λ_L .

The second step involves changes in the particle positions x_i with a fixed box length L . In this case, the gradient and second derivative terms reduce to

$$\frac{\partial \mathcal{H}}{\partial x_i} = \frac{\partial E}{\partial x_i}; \quad \frac{\partial^2 \mathcal{H}}{\partial x_i \partial x_j} = \frac{\partial^2 E}{\partial x_i \partial x_j}. \quad (10.51)$$

Therefore, this step is exactly the same as with our previous analysis for potential energy landscapes in the canonical ensemble. The position step vector is given by

$$\mathbf{h}_x = \sum_{i=1}^{3N} \frac{F_i}{\lambda_i - b_i} \mathbf{V}_i, \quad (10.52)$$

where b_i and $\mathbf{V}_i$ are the eigenvalues and associated eigenvectors of the symmetric $3N \times 3N$ Hessian matrix $\mathbf{H}$,

$$\mathbf{H}\mathbf{V}_i = b_i \mathbf{V}_i, \quad (10.53)$$

and F_i is defined by

$$\mathbf{g} = \sum_{i=1}^{3N} F_i \mathbf{V}_i. \quad (10.54)$$

The change in enthalpy associated with the position step vector $\mathbf{h}$ is

$$\Delta\mathcal{H}_x = \Delta E_x = \sum_{i=1}^{3N} \frac{F_i^2 \left(\lambda_i - \frac{b_i}{2} \right)}{(\lambda_i - b_i)^2}. \quad (10.55)$$

Again, the sign of the enthalpy change in a particular eigendirection $\mathbf{V}_i$ depends on both the eigenvalue b_i and the choice of Lagrange multiplier λ_i .

10.5 Choice of Lagrange Multipliers

In order to locate transition points and minima in the enthalpy landscape, we must make an appropriate choice of Lagrange multipliers. In this section, we specify a suitable choice of Lagrange multipliers for both cases.

10.5.1 Locating Transition Points

A transition point is defined as a stationary point where exactly one of the eigenvalues of the Hessian matrix is negative. Thus, a transition point corresponds to an enthalpy maximum in one eigendirection and an enthalpy minimum in all other eigendirections. With the split-step technique, the single negative eigenvalue may be any one of b_i or b_L . Treating the length dimension as the $(3N + 1)^{\text{th}}$ dimension, as in Equation (10.6), the eigenvector corresponding to $b_L = b_{3N+1}$ is

$$\mathbf{V}_L = \mathbf{V}_{3N+1} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix}. \quad (10.56)$$

As such, we may rewrite the total change in enthalpy as a summation of enthalpy changes in each of the $3N + 1$ eigendirections:

$$\Delta\mathcal{H} = \sum_{i=1}^{3N+1} \Delta\mathcal{H}_i, \quad (10.57)$$

where

$$\Delta\mathcal{H}_i = \frac{F_i^2 \left(\lambda_i - \frac{b_i}{2} \right)}{(\lambda_i - b_i)^2}. \quad (10.58)$$

Suppose we wish to find a transition point by maximizing enthalpy in a particular $\mathbf{V}_i$ eigendirection while minimizing in all of the orthogonal $\mathbf{V}_{j \neq i}$ directions. The eigendirection

$\mathbf{V}_i$ of interest may be associated with either changes in position or length. Due to the split-step nature of our approach, the eigenvector cannot have components of both position and length simultaneously. It follows from our previous analysis in Chapter 8 that a choice of $\lambda_i > |b_i|$ and $\lambda_j < -|b_j|$ would guarantee a step in the correct direction towards a transition point. However, this specifies neither the particular values of $\lambda_{i,j}$ nor the magnitude of the step.

We may simplify our analysis by assuming that a transition point search always starts from a local minimum in the enthalpy landscape. This is also the most practical case to consider from an applications point of view, since we are typically interested in finding the transition enthalpy between two stable configurations, e.g., two “inherent structures” using Stillinger’s terminology.¹⁷⁶ A minimum in the enthalpy landscape has the property $b_k > 0$ for all $k = 1, 2, \dots, N$. As we walk on the enthalpy landscape from the minimum to a transition point, we are essentially walking uphill along a “valley” or “streambed.” If the direction of our walk up the streambed is $\mathbf{V}_i$ and the step size is sufficiently small, we should have $b_j > 0$ for all $j \neq i$ and be near the enthalpy minima in the $\mathbf{V}_{j \neq i}$ directions along the entire walk. In the case of an infinitesimal step size, we would exactly follow the streambed; however, due to finite step sizes, we may have slight deviations from the streambed. These deviations may be corrected by an appropriate choice of $\lambda_{j \neq i}$, which is accomplished by finding the nearest stationary point in the $\Delta\mathcal{H}_{j \neq i}$ contribution:

$$\frac{\partial \Delta\mathcal{H}_{j \neq i}}{\partial \lambda_{j \neq i}} = 0 = -\frac{2F_{j \neq i}^2}{(\lambda_{j \neq i} - b_{j \neq i})^3} \left(\lambda_{j \neq i} - \frac{b_{j \neq i}}{2} \right) + \frac{F_{j \neq i}^2}{(\lambda_{j \neq i} - b_{j \neq i})^2}, \quad (10.59)$$

leading to

$$\frac{2 \left(\lambda_{j \neq i} - \frac{b_{j \neq i}}{2} \right)}{\lambda_{j \neq i} - b_{j \neq i}} = 1. \quad (10.60)$$

Therefore, we have

$$\lambda_{j \neq i} = 0. \quad (10.61)$$

The choice of $\lambda_{j \neq i} = 0$ reduces our Lagrange approach to exactly the Newton-Raphson method in all $\mathbf{V}_{j \neq i}$ eigendirections, and it is in agreement with our previous condition of $\lambda_{j \neq i} < b_{j \neq i}/2$ for minimization with $b_{j \neq i} > 0$. Note that if we accidentally step outside of the regime where $b_{j \neq i} > 0$, a negative $\lambda_{j \neq i} < b_{j \neq i}$ should be chosen. (This also indicates that the chosen step size in the $\mathbf{V}_i$ eigendirection is too large—so large that we have effectively stepped out of the streambed and started climbing hills in an orthogonal direction.)

The magnitude of the step size along the $\mathbf{V}_i$ eigendirection is given by

$$h_i^2 = c_i^2 = \frac{F_i^2}{(\lambda_i - b_i)^2}. \quad (10.62)$$

This leads to the condition

$$\lambda_i = b_i \pm \left| \frac{F_i}{c_i} \right|. \quad (10.63)$$

Since $\lambda_i > b_i$ is required for enthalpy maximization with $b_i > 0$, we choose

$$\lambda_i = b_i + \left| \frac{F_i}{c_i} \right| \quad (10.64)$$

for this case. If $b_i = 0$, we are at an inflection point and can simply take a step along $\mathbf{V}_i$

in the uphill direction.

As we progress up the streambed, eventually we will pass through an inflection point where b_i becomes negative. The condition for enthalpy maximization with $b_i < 0$ is $\lambda_i > b_i/2$. Since in this case the nearest stationary point is the transition point of interest with exactly one negative eigenvalue b_i , the most efficient choice of Lagrange multiplier is $\lambda_i = 0$, corresponding again to the Newton-Raphson step. Thus in the case of $b_i < 0$, the step size c_i is determined by the Newton-Raphson method.

Finally, we note that the first step from the initial minimum point must follow a different scheme than that given by Equation (10.62) since $F_i = 0$ for all i . In this case, we choose a simple step of magnitude c_i in the $\mathbf{V}_i$ eigendirection. There should be no components of $\mathbf{h}$ in the other $\mathbf{V}_{j \neq i}$ eigendirections since we also have $F_{j \neq i} = 0$ and wish to remain in the streambed.

10.5.2 Locating Minima

The steepest descent method fails to find minima in the tortuous enthalpy landscape of a bulk system within a reasonable computation time. Thus, we may modify the above eigenvector-following approach with a different choice of Lagrange multipliers in order to locate minima accurately. In order to find a minimum, we wish to minimize enthalpy in all eigendirections. Therefore, from Equations (10.57) and (10.58) we see that for $b_i > 0$, a choice of $\lambda_i = 0$ ensures enthalpy minimization. For all $b_i < 0$, we require $\lambda_i < b_i/2$. If we assume a step size of c_i in the $\mathbf{V}_i$ direction, then

$$c_i = \left| \frac{F_i}{(\lambda_i - b_i)} \right|. \quad (10.65)$$

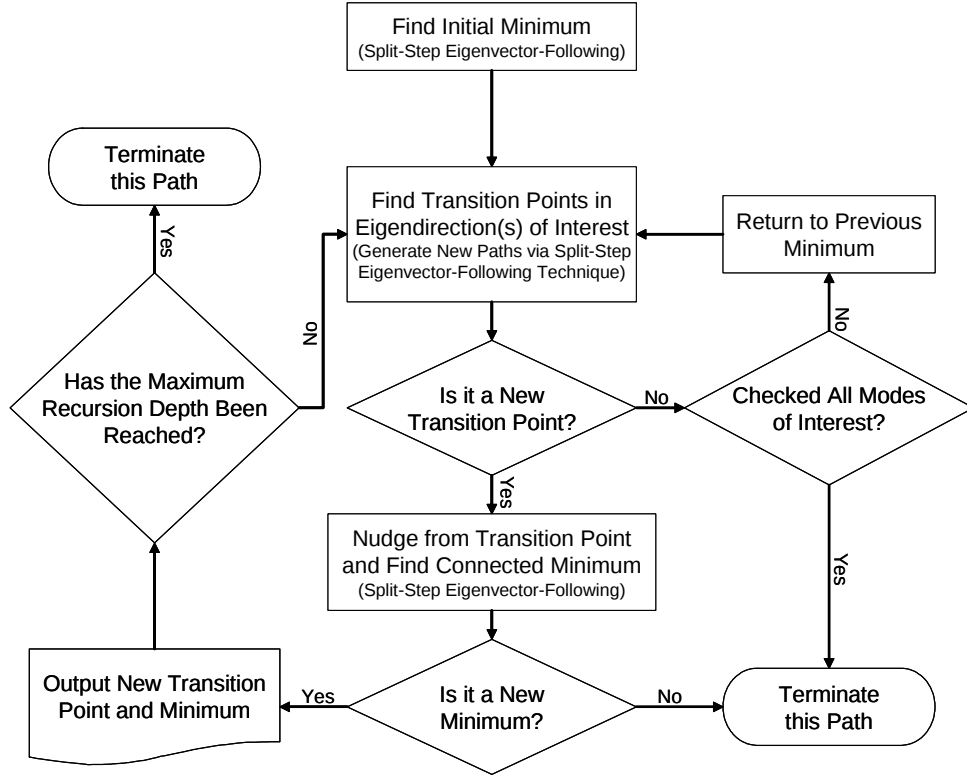


Figure 10.2. Flow chart of the recursive algorithm for mapping an enthalpy landscape.

Therefore, we choose

$$\lambda_i = b_i - \left| \frac{F_i}{c_i} \right|. \quad (10.66)$$

Finally, if $b_i = 0$, we are at an inflection point. In this case, we can simply take a step along $\mathbf{V}_i$ in the downhill direction. We have found this technique to be much more effective than steepest descent for finding minima in a bulk system.

10.6 Recursive Algorithm for Mapping the Enthalpy Landscape

A recursive algorithm for mapping an enthalpy landscape using split-step eigenvector-following is given in Figure 10.2. The actual split-step eigenvector-following technique is executed every time a new minimum or transition point needs to be found. The split-step technique itself is outlined in Figure 10.1 and executed iteratively according to the following procedure:

1. If finding a transition point, choose the eigendirection of interest to follow. This may be along the parallel or antiparallel directions of the softest mode, or along any of the harder modes of interest.
2. Execute a change in the length L of the simulation cell while maintaining constant normalized positions $\bar{x}_i$. Compute the first and second derivatives of enthalpy with respect to length, F_L and b_L , and choose a Lagrange multiplier according to the criteria put forth in Section 10.5. Change the simulation cell length in three dimensions by the resulting step h_L .
3. Change the atomic positions x_i while maintaining constant L . Compute the gradient $\mathbf{g}$ and Hessian $\mathbf{H}$, and determine the eigenvalues and normalized eigenvectors of the Hessian matrix. The eigenvectors form the columns of a $3N \times 3N$ unitary matrix:

$$\mathbf{U} = \begin{pmatrix} \mathbf{v}_1 & \mathbf{v}_2 & \cdots & \mathbf{v}_{3N} \end{pmatrix}. \quad (10.67)$$

Compute the vector $\mathbf{F} = \mathbf{U}^\top \mathbf{g}$, where

$$\mathbf{F} = \begin{pmatrix} F_1 \\ F_2 \\ \vdots \\ F_{3N} \end{pmatrix}. \quad (10.68)$$

Select the Lagrange multipliers λ_i according to the criteria in Section 10.5 and compute the step vector $\mathbf{h}$. Update the atomic positions accordingly.

4. Repeat steps 2-3 until converged at a minimum or transition point. The criteria for convergence are: (a) $|F_i| < \epsilon$, where ϵ is chosen to reflect the desired level of precision; and (b) all $b_i > 0$ for a minimum or exactly one $b_i < 0$ for a transition point.

10.7 Partial Enthalpy Landscape of Selenium

We have implemented this algorithm and tested it for a 64-atom selenium system with periodic boundary conditions using our *ab initio* potentials from Part I. The split-step eigenvector-following technique was able to correctly find both minima and transition states in the Se_{64} enthalpy landscape. Two example minima and the connecting transition state are shown in Figure 10.3. A partial disconnectivity graph of the Se_{64} enthalpy landscape is shown in Figure 10.4, showing a total of 70 minima and their connecting transition points. The disconnectivity graph was generated using software by Mark A. Miller.²³⁹

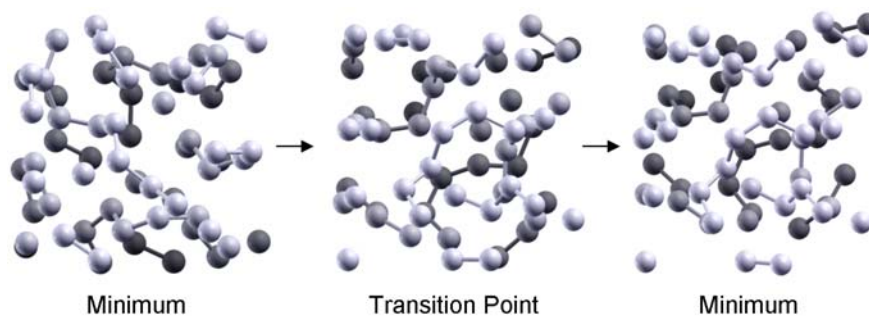


Figure 10.3. Example minima and transition point in the enthalpy landscape of Se_{64} , assuming periodic boundary conditions.

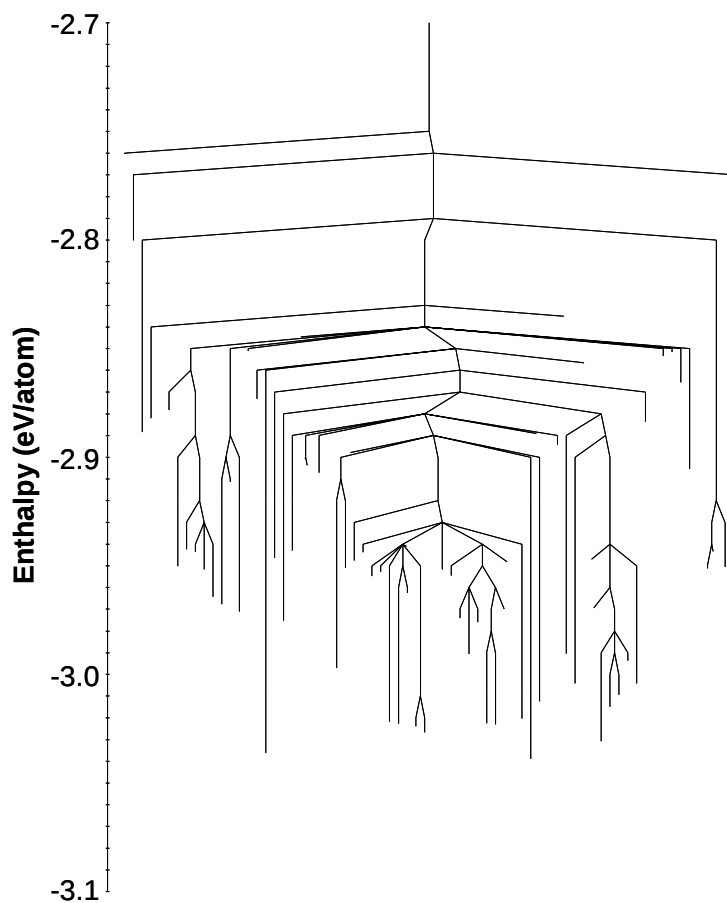


Figure 10.4. Partial enthalpy landscape of a 64-atom selenium system, assuming periodic boundary conditions.

10.8 Volume-Temperature Diagram for Selenium

We use the partial enthalpy landscape of Figure 10.4, together with our glass transition model of Chapter 7, to compute a preliminary volume-temperature diagram for selenium, as shown in Figure 10.5 assuming linear cooling. The transition frequencies ω_α in Equation (7.20) are computed from the corresponding eigenvalues b_α by

$$\omega_\alpha = \sqrt{\frac{b_\alpha}{m}}, \quad (10.69)$$

where m is the atomic mass.

While the molar volumes in Figure 10.5 are not yet quantitatively accurate due to the small sampling of inherent structures (the liquid at 500 K should be about 19.5 cm³/mol, and the glass at 300 K should be closer to 18.5 cm³/mol⁷⁹), the glass transition does occur in the correct temperature range for selenium. In addition, we observe the correct trend that a faster cooling time (1 ns in Figure 10.5) yields a glass with a higher molar volume than a slower cooling time (2 ns). The slopes of the two volume-temperature curves are nearly identical in the glassy regime, indicating similar thermal expansion coefficients for the two glasses. Finally, Figure 10.6 shows that selenium glass does not retrace its cooling path upon reheating. This figure also shows that reheating and subsequent recooling lead to a different final molar volume of the glass. A more thorough mapping of the enthalpy landscape is necessary in order to compute a quantitatively accurate volume-temperature diagram for selenium.

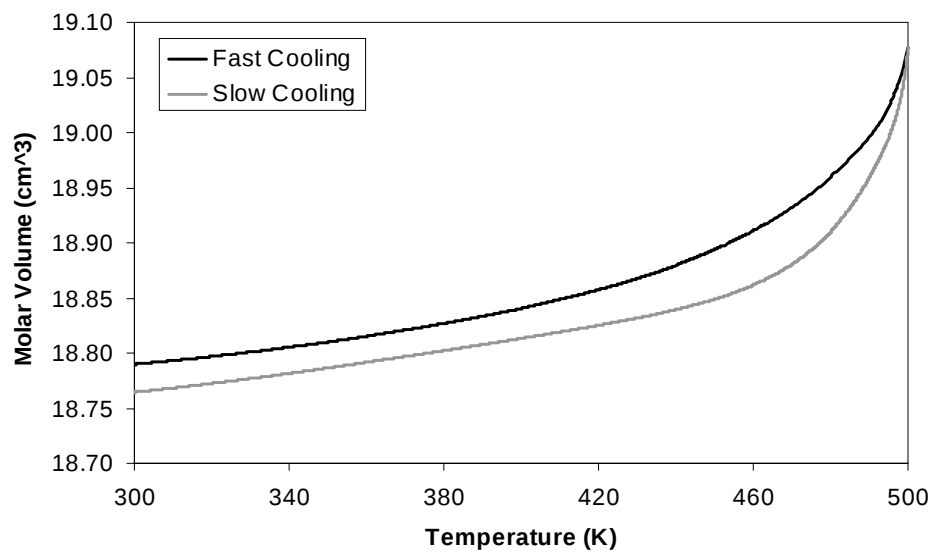


Figure 10.5. Computed volume-temperature diagram of selenium.

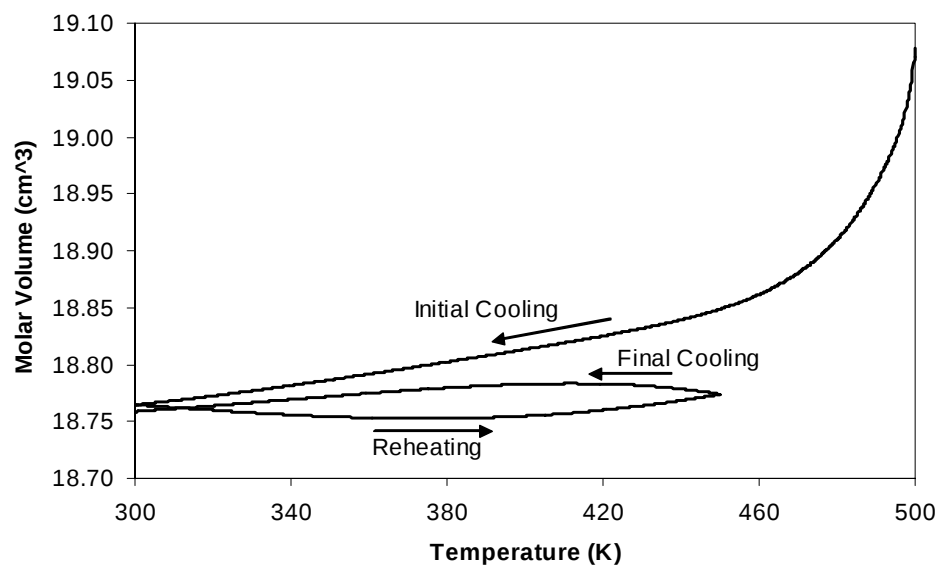


Figure 10.6. Volume-temperature diagram of selenium showing reheating and subsequent recooling. The final glass volume is less than that of the initially cooled glass.

10.9 Conclusions

In conclusion:

- We have derived the first-ever set of *ab initio* potentials for chalcogenide systems, including two-, three-, and effective four-body terms.
- We have developed Molsym, a flexible object-oriented platform for classical atomistic simulations.
- Using the Metropolis Monte Carlo technique and our *ab initio* derived potentials, we have computed the structure of elemental, binary, and ternary chalcogenide glasses.
- We have investigated rigidity percolation, elasticity, and incipient plasticity in chalcogenide glasses at the atomistic level.
- We have shown the first-ever support of the Phillips-Thorpe theory of topological constraints based on *ab initio* physics.
- We have derived a new model of glass transition range behavior based on nonequilibrium statistical mechanics and an inherent structure approach.
- We have demonstrated for the first time the connection between energy landscape topology and supercooled liquid fragility.
- We have developed new eigenvector-following techniques for locating minima and transition states in potential energy and enthalpy landscapes.
- We have mapped the inherent structures and transition states of elemental and heterogeneous chalcogen clusters.

- Using our *ab initio* derived potentials, split-step eigenvector-following technique, and new model of the glass transition, we have computed the first-ever volume-temperature diagram of a glass-forming system without any experimental inputs.

Future work will focus on the statistics of enthalpy landscapes for glass-forming systems in order to compute quantitatively accurate volume-temperature diagrams for realistic glass-forming systems.

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