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Towards the Physical Origin of Flexible-to-Rigid Transition in $\text{Ge}_x\text{Se}_{1-x}$ Glass

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Civil Engineering

by

Zhangji Zhao

2024

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ABSTRACT OF THE DISSERTATION

Towards the Physical Origin of Flexible-to-Rigid Transition in $\text{Ge}_x\text{Se}_{1-x}$ Glass

by

Zhangji Zhao

Doctor of Philosophy in Civil Engineering

University of California, Los Angeles, 2024

Professor Ertugrul Taciroglu, Chair

Based on their connectivity, network glasses can be classified as flexible, stressed–rigid, or isostatic, if the number of topological constraints is lower, larger, or equal to the number of atomic degrees of freedom, respectively. Thanks to the absence of any stoichiometric requirement, the rigidity of glasses can be continuously tuned (e.g., from flexible to stressed–rigid) by changing their chemical composition. Interestingly, optimally-constrained isostatic glasses have been noted to exhibit unusual properties (e.g., nearly-reversible glass transition, low relaxation, desirable mechanical properties, etc.). Especially, the non-aging intermediate state features an almost vanished endotherm between the first and second heat scan across glass transition, providing a pathway for phase change material optimization in the application of non-volatile rewriteable media. However, the physical origin of the unusual behaviors and properties of isostatic glasses remain unclear.

This thesis begins with investigating how the flexible-to-rigid transition in network glasses is encoded in their energy landscape based on molecular dynamics simulations. To this end, we introduce a simplified, yet realistic model of network glasses with varying connectivity. We characterize the topography of these glasses by adopting the activation-relaxation technique (ART), which enables a systematic search of saddle points and transition pathways in the energy landscape surface. We then demonstrate that the flexible-to-rigid transition arises from an interplay between low-energy saddle points (in flexible glasses) and topological frustration (in stressed-rigid glasses). Also, by utilizing the ring structure, we expand the transition correlation with ring size distribution. Meanwhile, we highlight the local heterogeneity with all the energy landscape features by dicing the model into small cubes. Comparing within a single glass helps exclude the effect of different configurations, further consolidating our conclusion on the physical origin of rigidity transition.

Finally, to explore the role of chemistry effect in rigidity transition, we compare the behavior of the simple connectivity model with a realistic $\text{Ge}_x\text{Se}_{1-x}$ model. With the similar shape of enthalpic differences, the realistic model could reveal the effect of glass-forming ability with experimental results where the simple model fails. Overall, we have a clear pathway towards understanding the physical origin of rigidity transition of $\text{Ge}_x\text{Se}_{1-x}$ glass.

The dissertation of Zhangji Zhao is approved.

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2024

To my parents

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Publications:

1. **Zhao Z**, Liu H, Smedskjaer MM, Bauchy M. “Energy Landscape Signature of the Flexible-to-Rigid Transition in Network Glasses”. (*In progress*)
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Chapter 1. Introduction

1.1 Phase Change Materials

Phase-change materials (PCMs) are a highly promising candidate for next-generation non-volatile memory (NVM) devices, offering potential performance improvements over flash memory with outstanding scalability. Effective utilization of PCMs in high-performance applications necessitates achieving fast write and read times while concurrently maintaining superior data retention characteristics. Furthermore, it could serve as a viable replacement for NOR flash, offering enhanced scalability. How PCMs encoding and retaining data are based on the electrical resistance between crystalline and amorphous phases. When cooled from temperatures surpassing the material's melting point, PCM is quenched into a glassy, amorphous state. Conversely, cooling from temperatures between crystallization and melting points induces a crystalline configuration. Joule heating is triggered by either electrical or optical pulses, and the nanosecond-scale transition speed between these two phases renders it an optimal medium for memory devices.

One of the most promising alloys is the GeSbTe (GST) pseudo-binary, consisting of Sb_2Te_3 and GeTe, which has been widely studied in electrically switched memory materials. Figure 1-1 shows the tertiary GST phase diagram with some popular phase change alloys highlighted. However, GST maintains certain unfavorable characteristics, including a high melting point, comparatively low crystallization temperature, and activation energies. Meanwhile, the biggest issue comes from the nature of the amorphous state as resistance drift. The drift process involves a continual rise in the resistivity of the amorphous phase, tied to the structural rearrangement of

the amorphous chalcogenide and the dynamics of intrinsic traps. It has been shown that the resistance drift follows a power law that increases with time. This hampers the storage capacity for multilevel memory devices as the drifted resistance may overlap.

To overcome these issues, several elements have been studied for doping into GST systems such as C, N, O, Mn, Fe, Zn and Mo, to enhance the performance of GST materials. Exploring innovative systems often entails substantial trial and error, primarily due to the conflicting requirement for robust amorphous-phase stability alongside rapid crystallization rates. Consequently, enhancing GST properties through doping has emerged as another extensively explored avenue of research. High crystallization speed, high resistance difference between phases, and low resistance drift need to be satisfied at the same time. Thus, to better optimize PCMs, it is important to understand the physical origins for corresponding properties and MD simulation has proved to be a cost efficiency tool to provide valuable insights into structural features, compared with ab initio molecular-dynamics (AIMD) simulations.

In this study, we start with a generic network model and further extend to a realistic $\text{Ge}_x\text{Se}_{1-x}$ glass model. The realistic $\text{Ge}_x\text{Se}_{1-x}$ glass model shows superior structural features and better computational efficiency over ab initio simulation. The effect of the fine structural for $\text{Ge}_x\text{Se}_{1-x}$ glass such as homopolar bond, heteropolar bond and edge-sharing can be better revealed from the empirical $\text{Ge}_x\text{Se}_{1-x}$ glass model. Although $\text{Ge}_x\text{Se}_{1-x}$ glass has been extensively studied during the past decades, the model could still serve as a baseline for element doping or pseudo-binary mixture for the compositional searching for PCMs optimizations.

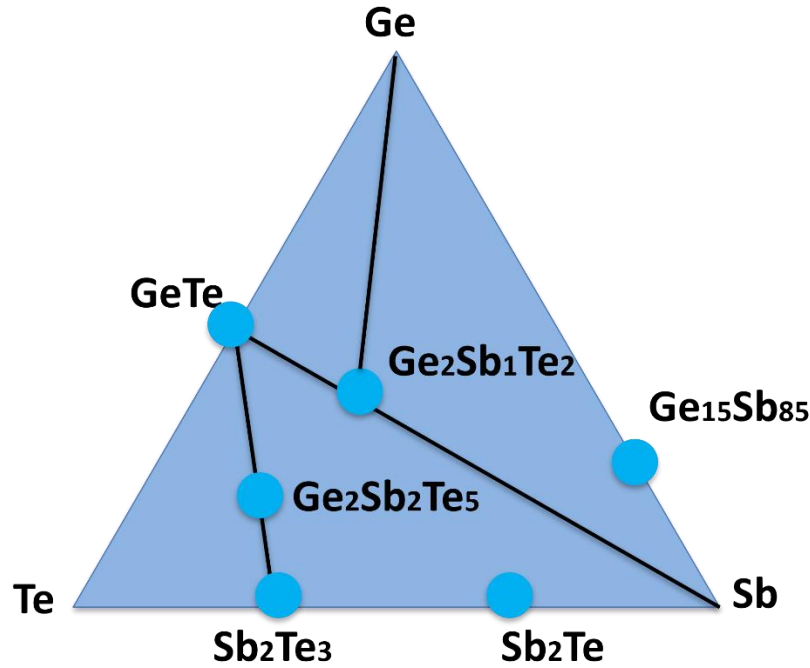


Figure 1-1: Tertiary Ge-Sb-Te phase diagram with some popular phase change alloys highlighted.

1.2 Molecular dynamics (MD) simulation

The molecular dynamics (MD) simulation is based on the interatomic forcefield to predict the atomic motion trajectories according to Newton's law of motion. It is the main difference compared with other types of simulation, such as Monte Carlo (MC) or reverse MC simulations, which only rely on the target objective (e.g., minimizing structural energy or the discrepancy with experimental results). The main advantage of MD simulation is the access to all the structural information that can be checked with experimental data. Although MD simulation predicts the instantaneous atomic motions in glasses, it is limited to short timescales (up to a few nanoseconds) compared to the experimental timescale (up to days). Note that direct comparison

with experiment is still possible for equilibrium or metastable state since the system structure or glass properties do not depend on their thermal history.

The algorithm of MD simulation relies on a four steps loop. Based on the selected interatomic potential, along with atomic coordinates r_i , the potential energy for $U(\{r_i\})$ can be computed. Then the resultant force F_i can be calculated via their time derivative, given by $F_i = -\partial U(\{r_i\})/\partial r_i$. The second derivative leads to the acceleration $a_i = F_i/m_i$, where m_i is the mass of atom i . Finally, after a small fixed timestep, the new atom positions would be updated via Verlet or leapfrog algorithm and the trajectory of each atom can be obtained by looping these four steps.

When applying MD simulation to glass systems, the most critical points are the choice of interatomic potential and the timestep. The forcefield needs to accommodate with the glass structure or target properties to be calculated. The timestep needs to be small enough ($\sim 1\text{fs}$) to ensure the accuracy of the numerical integration. If the integration timestep is small enough, the simulation accuracy is primarily dependent on the forcefield.

The most used glass preparation method is mimicking the melt-quenching experimental process, which cools the glass from an elevated temperature at a predetermined rate. It starts with an initial cubic box and generally the atomic arrangement of the starting configuration (avoid unrealistic overlapped atomic coordination) does not affect the result if the system fully turns into liquidus (fully reset) at high temperatures. Then, the thermodynamic ensemble needs to be selected from microcanonical (NVE), canonical (NVT) and isothermal-isobaric (NPT) ensembles. In our case, mainly due to the compatibility of the selected forcefield, we want the system box size to stay constant, the melt is quenched in NVT ensemble by linearly decreasing the

temperature over time with sufficient cooling rate. The cooling rate for MD simulation is typically in the range of 10^{14} - 10^9 K/s, compared to 10^2 – 10^0 K/s in experiments. Once the relaxation is finished and glass is formed, investigations can be applied to the final configuration, including structural, mechanical, thermodynamic, and vibrational/dynamical analysis.

1.3 Topologically constrained theory and isostatic state

Owing to the nanocrystalline and nonequilibrium nature of glass, applying first principles modeling to predict glass properties is not cost effective and can only handle small scale simulation. To accelerate the modeling, topological constraint theory (TCT) has been successfully applied to predict glass properties and explain glass forming process. The complex network glass structure is simplified by nodes and mechanical trusses, and it thus sufficiently captures the atomic topology that governs the macroscopic property while disregarding less relevant second-order details. TCT has shown the existence of a flexible to rigid stability transition, as the function of number of constraints. How constraint is quantified is described in the following.

Under TCT, covalent bonds are analogized to mechanical constraints, imposed by radial bond stretching (BS) and angular bond bending (BB). The value of BS and BB constraints applied on an atom can be calculated from its coordination number r . Since each radial constraint is shared by two atoms and the value of BS is given by $r/2$. For the BB constraint, a triplet requires 1 BB constraint, and each additional bond adds 2 more BB constraint, and thus given by $2r - 3$ ($r \geq 2$). So, the total number of constraint (nc) is expressed by $nc = BB + BS = 5/2 \langle r \rangle - 3$.

Based on the Maxwell stability criterion, an intermediate level of constraint state can be identified, during the transition from a freely deformed network to a highly connected stressed-rigid structure. As we know, the available degree of freedom (nd) per atom equals to 3 in a three-dimensional atomic structure, which means when nc per atom also equals to 3, $nc = nd$, then the structure reaches a rigid (free of floppy modes) but unstressed state. If we want to expand TCT to an N atoms system, the system nc would be the summation of BB and BS , over number of atoms N , leading to a single isostatic threshold for the whole glass where $nc = 3$. However, this mean-field approach of TCT cannot capture the effect of local heterogeneity variability, in another word, the single threshold value only valid for ideal homogenous glass. Note that, isostatic state is characterized by the glass enthalpy of relaxation instead of theoretical constraints counting. Boolchand proposed and showed that the isostatic state can be achieved within a continuous compositional range, instead of a fixed threshold. The isostatic, or intermediate region can be then identified by the two transitions: flexible-to-rigid transition and unstressed-to-stressed transition. Due to the superior emergence of minimum enthalpic relaxation, the isostatic region also known as reversibility window, has been demonstrated both experimentally and computationally in many glasses. The existence of reversibility window draws much attention due to various remarkable properties such as superior resistance to creep, fracture toughness and irradiation resistance. These properties originate from the optimal relaxed structure of isostatic state and the key to decode the optimal relaxation process is the enthalpy landscape.

Meanwhile, it is still unclear the physical origin of intermediate state and its structural signatures. Since thermally reversing glass transition always exhibits within a certain range of connectivity, despite chemical composition. One explanation suggests that the spatial distribution of

connectivity could be the key, as it may lead to a self-organization of the network, becoming rigid while preventing internal stress accumulation.

Here is a simple analog to understand how the connectivity governs the isostatic state. We can treat atomic connectivity as social network connection. If the social network is loosely connected, people would hardly feel each other and cannot get support inside this network. But if people are so tightly connected, everyone is highly related to each other, the relationship network would over-stressed. So there exists an ideal level of connection, that people get enough support while not being bothered by stress from the social network. That is the isostatic state in the case of atomic structure.

1.4 Thesis organization

Since our goal is to understand the phenomena of isostatic state in network glass, this thesis starts with building a generic model that can replicate isostatic state. Then the corresponding structural signatures are carefully investigated to get their correlation. Local heterogeneity is further discussed to consolidate our conclusions and provide a new approach to study structural heterogeneity. After concluding the physical origin of isostatic state in the simplified model, we continued to develop a realistic $\text{Ge}_x\text{Se}_{1-x}$ glass model, which has the same fashion of bonding feature as the toy model. We can then highlight the effect of fragility of the realistic $\text{Ge}_x\text{Se}_{1-x}$ glass model compared to the simplified model.

To elucidate the physical nature of isostatic state, the thesis is organized as follows:

In Chapter 2, we build a simple network glass model after examining previous glass modeling studies. Our target structure is an AB mixture with 2-folded and 4-folded bonding features. Stillinger-Weber interatomic potential is a suitable forcefield as it includes 2-body radial and 3-body angular term. The MD simulation is carried out using Largescale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package. The coordination and fraction of bonds analysis finally endorses the model rationality as a network glass model. After comparing with classical bonding models, our model shows a decent balance between the over simplified models of random covalent network (RCN) and chemically ordered network (CON). Without embedded chemistry, the model shows the ability to capture the effect of connectivity while keeping the simplicity.

In Chapter 3, based on this simple model, we extend our exploration to the energy landscape signatures of flexible to rigid transition in network glass under various connectivity. The U shape of enthalpic differences as the function of connectivity is reproduced, identifying the existence of isostatic state. Meanwhile, we characterize the energy barrier of these glasses by adopting the activation-relaxation technique (ART), which applies a local perturbation to probe local saddle points. We then demonstrate that the flexible-to-rigid transition arises from an interplay between floppy modes and highly stressed structure. Also, by utilizing the ring structure, we expand the transition correlation in medium range. All the energy landscape signatures, including MSD, stress/atom, energy barrier and ring, all display striking minima corresponding to a certain window of connectivity.

Meanwhile, to further consolidate our conclusion and highlight the structural heterogeneity, we examine the local energy landscape signature by dicing one glass into many small cubes. In this

case, the sampling size is greatly increased to cover more configurations with more nc values. A more distinct reversibility window is revealed with a clear sudden slope of change between the two transitions. Also, the local energy landscape analysis shows that the energy barrier reaches the maximum where ring size = 6. It indicates that the structure is stress-free when ring size equal to 6, which has been validated in silica both experimentally and computationally. The relationship between E_b and ring size reinforced the optimal relaxation of the isostatic state, also corresponding with the medium-range order of atomic interaction.

In Chapter 4, we build a realistic empirical Ge_xSe_{1-x} model, with the help of machine learning parameterization. The particle swarm optimization (PSO) is first applied for a rough estimate, and the Bayesian optimization is then applied for a more accurate parameter search. The ab initio results of Ge_xSe_{1-x} glass pair distribution function (PDF) is used for reference and the cost function is defined as the root mean square deviation (RMSE) between reference and empirical PDF. Since the simple model uses the same Stillinger-Weber potential as the realistic Ge_xSe_{1-x} model, we compare these two models' signatures to extract the effect of the realistic forcefield parameterization. This set of parameters also stands for the chemistry effect of realistic Ge_xSe_{1-x} glass, while is not included in the simple model. The experimental result of effect of fragility is replicated by the realistic Ge_xSe_{1-x} model, owing to capturing the trend of T_g while the simple model fails.

1.5 Contribution

To sum up, the contribution of this thesis is as follows:

1. We developed the first generic model for network glass in MD simulation.
2. We first demonstrated generic energy landscape signatures for network glass in MD simulation.
3. We first directly illustrated the role of energy barriers in the process of flexible to rigid transition in network glass.
4. We first illustrate the glass relaxation in the medium-range order, which can be achieved by changing small-size rings.
5. We first developed the empirical $\text{Ge}_x\text{Se}_{1-x}$ model with MD simulation and matched the effect of fragility with experimental results.

Chapter2. A generic model of network glass with tunable connectivity

2.1 Introduction

In pursuing future non-volatile recordable and rewritable media, phase change material (PCM) is one of the most promising candidates with various supremacies, such as fast switching in nanoseconds, low voltage, better scalability over flash memory and so on [1-4]. By swapping PCM solid-state phases, information can be stored based on the pronounced electrical contrast between insulating amorphous and conductive crystalline states. The phase manipulation is always accomplished by the Joule heat induced by an electrical or optical pulse [5]. However, the off-equilibrium nature of the glassy state continuously drives the material towards further structural relaxation, leading to the resistance drift [6, 7]. Once drifted, the amorphous state could not retrieve the same resistivity after a prolonged cooling and reheating cycles, hampering the storage density and lifetime of a PCM patterned memory device. Thanks to the discovery of the thermally reversing glass transition [8-10], known as intermediate phase, displays a near-zero structural relaxation(endotherm) between first and second heat scan across glass transition. The reversibility region always exhibits within a certain range of connectivity, despite chemical composition, as studied both experimentally and computationally [11]. The stress-free, quasi-equilibrium intermediate phase provides a pathway towards PCM optimization.

To elucidate the physical origin of intermediate phase, a proper microscopic model is essential. Efforts have been made by simplifying bonding network into nodes and lines, known as triangular lattice model [12, 13]. It converts the actual atomic structure to a pure topological geometry, and successfully in retrieving glass dynamics, such as glass transition and rigidity

percolation [14, 15]. However, the application of those simplified models is limited due to the lack of realistic chemical interactions and corresponding dynamical process [16].

As an alternative approach, molecular dynamics simulation can capture the trajectory of individual atoms with realistic atomic interactions, and hence could provide more comprehensive insight into the physical process. To this end, some generic atomic models have been proposed, such as the Kob-Andersen Lennard-Jones (KALJ) binary mixture [17], which could provide an efficient route to achieving a universal understanding in the field of glass physics, including phase transition [18], crystallization [19], viscous liquid and glass transition [20]. The insight obtained from those generic models could also be used to understand the physical behavior of real glasses [21, 22]. Nevertheless, in the context of networks, the KALJ model appears insufficient due to its absence of critical factors, such as low coordination number (CN), directional bond, and most crucially, the capacity to modify overall connectivity.

In this study, we introduce a generic model of a 2-fold and 4-fold coordinated binary network, notable for connectivity tunability, in molecular dynamics (MD) simulation. To initiate, the model is designed with requisite simplicity to effectively capture physical processes, while simultaneously preserving the realism to retain the tetrahedra motif as the basic building block. This is realized by considering 2-body interatomic and 3-body angular terms, recognized as the hallmark of Stillinger-Weber potential. Details regarding the forcefield parametrization for enhanced generality will be further discussed. The result section is organized as follows: firstly, the model was demonstrated to exhibit glass-like behavior under different temperatures and corresponding states. Subsequently, we showed that overall connectivity tunability is achieved by varying the composition ratio. By comparing the predicted bond statistics from our model

with established ideal network models, we find that the formation of A-A bonds is not forbidden at low concentration of A atoms. However, the suppression of A-A bond formation is observed when the fraction of A atoms reaches 20%. As we examined the model to be a proper description of 2-fold and 4-fold coordinated AB mixture, it can be further applied to investigate the physical behavior of network glasses, even extended to any topological issues such as neural networks [23,24].

2.2 Methods

Parameterizing interatomic potential

In the following, the forcefield parameterization is detailed as follows. To begin with, we choose Stillinger-Weber (SW) potential as our forcefield, since it is the simplest analytical potential form considering long range interaction term and angular term [25, 26]. The potential is described as the summation of a 2-body and 3-body part, given by:

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

$$\phi_2(r_{ij}) = A_{ij} \epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp \left(\frac{\sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right)$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \epsilon_{ijk} [\cos \theta_{ijk} - \cos \theta_{0ijk}]^2 \exp \left(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \exp \left(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}} \right)$$

where the subscripts ij , ik , and ijk represent pairs and triplets involving atoms i , j , and k , correspondingly. ϵ and σ are the energy and distance scaling parameters, respectively. A , B , p , q , λ and γ are fitting parameters for 2-body and 3-body interatomic distances and angles. The 3-body angular term attains tetrahedral geometry (109.5 degree).

The model is based on a binary AB mixture with both types of atoms sharing the same mass. Without losing generality, we applied reduced LJ unit and the fundamental quantities including mass, distance scaling parameter σ , energy scaling parameter ϵ , and Boltzmann constant $k_B = 1$. For 2-body parameters, the values of A, B, p, q, γ and a_{ij} are taken from the standard SW parameters, as shown in table 2-1(a). The standard SW parameters are selected to ensure the diamond atomic structure is the most stable arrangement at low pressure, while maintaining a reasonable agreement with experiment on melting point and structure in liquidus phase [27]. To prevent discontinuities artifacts during simulations, the potential automatically cuts off at $r = a_{ij}$, as illustrated in Figure 2-1(a). For 3-body parameters, as shown in table 2-1(b), the energy penalty parameter λ_{ijk} of X-A-X (A atom centered) is set larger than X-B-X (B atom centered) to provide a higher energy cost between A atoms, keeping A atoms from congregation and ending with a more uniform distribution. The tetrahedral angle of X-A-X equals to 109.5 degrees and the two-bonded chain angle of X-B-X is set as 160 degrees to minimize 3-bonded B atoms, as shown in Figure 2-1(b).

Table 2-1. (a) Values of parameters for the 2-body energy term of SW potential

2-body parameters								
i-j	ϵ_{ij}	σ_{ij}	a_{ij}	γ_{ij}	A_{ij}	B_{ij}	p_{ij}	q_{ij}
A-A, B-B, A-B	1	1	1.8	1.2	7.049556277	0.6022245584	4	0

Table 2-1. (b) Values of parameters for the 3-body energy term of SW potential

3-body parameters			
i (center)-j-k	ϵ_{ijk}	λ_{ijk}	$\theta_{ijk} (^{\circ})$
X-A-X	1	44	109.5
X-B-X	1	37	160

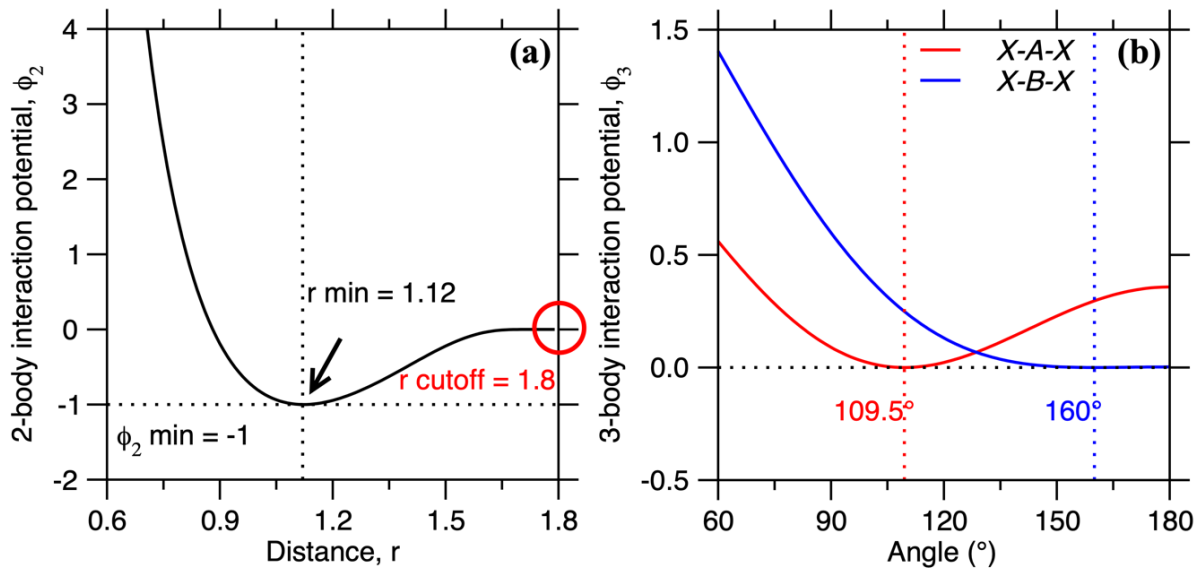


Figure 2-1: (a) 2-body A-A, A-B, B-B interaction potential. (b) 3-body interaction potential for X-A-X and X-B-X, as a function of bond angle.

Classic MD simulation

Adopting the previously presented model, we simulate the AxB_{1-x} binary with molecular dynamics (MD). The classical MD simulation is carried out using Largescale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [28] in canonical NVT ensemble. The simulated system comprises 8527 atoms placed in a periodic cubic simulation box. To obtain a relaxed configuration, we adopt a conventional melting-quenching procedure. In detail, the configuration is obtained by quenching the random atomic structure from high temperature (i.e., $T = 0.3$) to $T = 0$ with a cooling rate of 0.05. Note that all quantities are unitless under LJ unit. A Nosé–Hoover thermostat [29] is used through all simulations.

2.3 Results and discussion

Configurations under different temperature

To identify the glass features, we take AB_4 as an example. As shown in Figure 2-2(a), an evenly distributed AB mixture can be observed without obvious clustering and crystallization. The tetrahedral structures of 4-bonded A atoms and the chains/rings form 2-bonded B atoms are shown in the inset as expected. When the configuration relaxed from liquidus state, the energy and pressure decrease monotonically with decreasing temperature. The slope of curve suddenly changes when $T = 0.06$, which suggests the emergency of the dynamical arrest, as shown in Figure 2-2(b). Figure 2-2(c) shows the pressure eventually reached zero with the decreasing temperature in NVT ensemble. The total pair distribution function (PDF) [30] of AB_4 indicates a disordered arrangement of the configuration, as shown in Fig. 2(d).

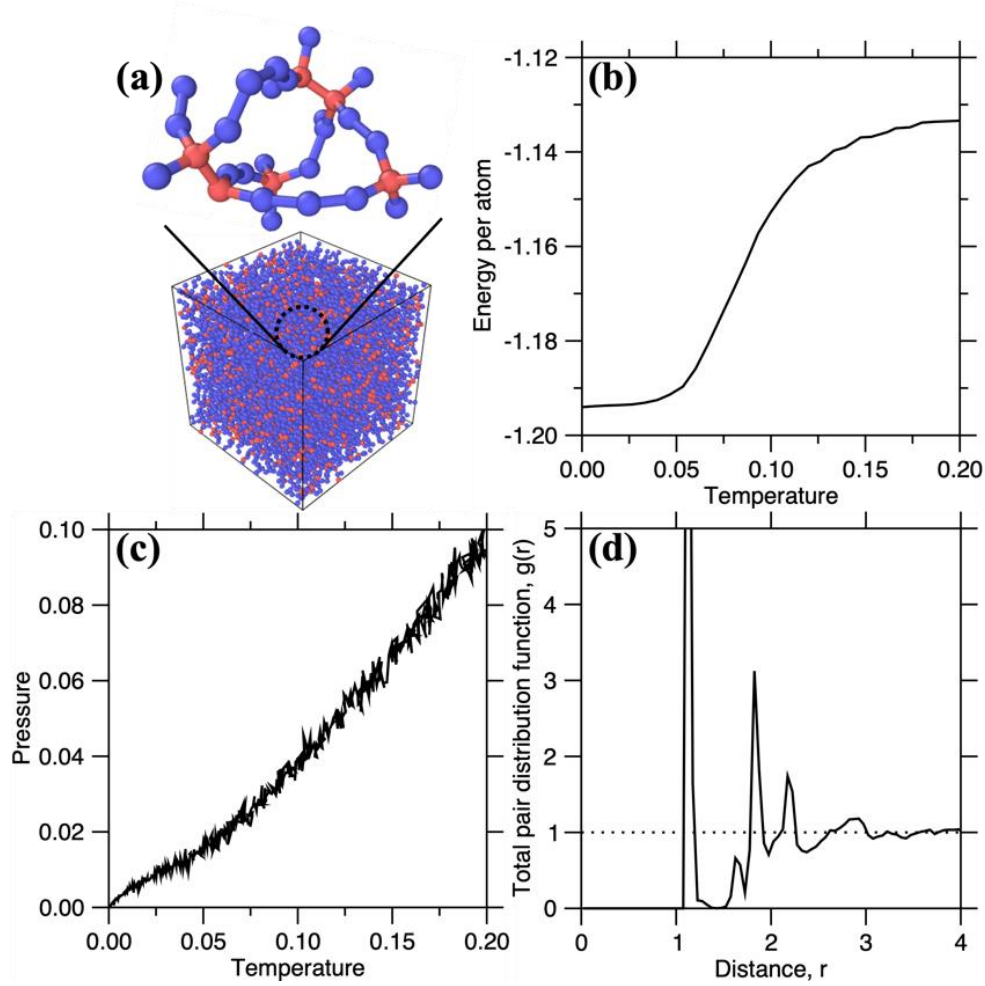


Figure 2-2: (a) Snapshots of AB_4 configuration, the inset shows the 4-fold coordinated A atom (red) and 2-fold coordinated B atom (blue) of the glass. (b) Energy and (c) pressure evolution during cooling. (d) Total pair distribution function.

Then we explore the structure of the system under states of liquid, supercooled liquid, and glass. Partial PDF of AB_4 is computed at corresponding temperatures as shown in Figure 2-3. The first partial PDF peak positions denote the short-range order of A-A, B-B and A-B bonds are $r = 1.135, 1.123$, and 1.123 , respectively, which indicates the bond length of all types of bonds are about the same. As shown in Figure 2-3, the first coordination peak of A-A bond is broadened

compared to A-B and B-B, mainly due to the higher structural distortion of A-A bonding structure. The partial PDF peaks under higher temperatures have lower intensity and broader width, mainly associated with the thermal breakage of the underlying constraint and thermally induced randomness. Similarly, as shown in Figure 2-4, the angle distribution peaks of X-A-X and X-B-X are narrowed as the temperature decreases, eliminating the thermal effect on angular constraint. For X-B-X, the first peak around 120 degrees and second peak around 160 degrees correspond to three- and two-coordinated B atom bonding structures, respectively. We observe that the bonding migration under different states follows the trend of glass-forming process, and we can thus confirm that our model reproduces a reliable glass simulation.

Finally, we examine the coordination distribution of the glass structure. As shown in Figure 2-5, 99.1% of A atoms are four-coordinated and 95.8% of B atoms are two-coordinated. The average coordination number (CN) of A and B atoms are 3.99 and 2.07, respectively, close enough to the ideal case of a 2- and 4-coordinated mixture. By now, our model has been confirmed to provide a proper description of an AB binary network glass structure. More connectivity tuning capability and characterization are described in the following.

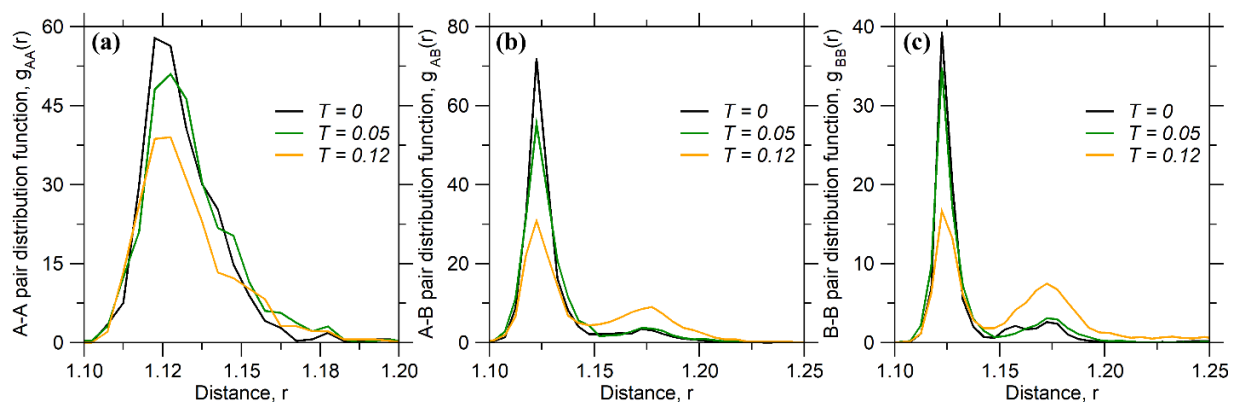


Figure 2-3: Partial PDF between A-A, A-B and B-B atoms at liquidus state ($T= 0.12$), around transition temperature ($T= 0.05$), and glassy state ($T=0$).

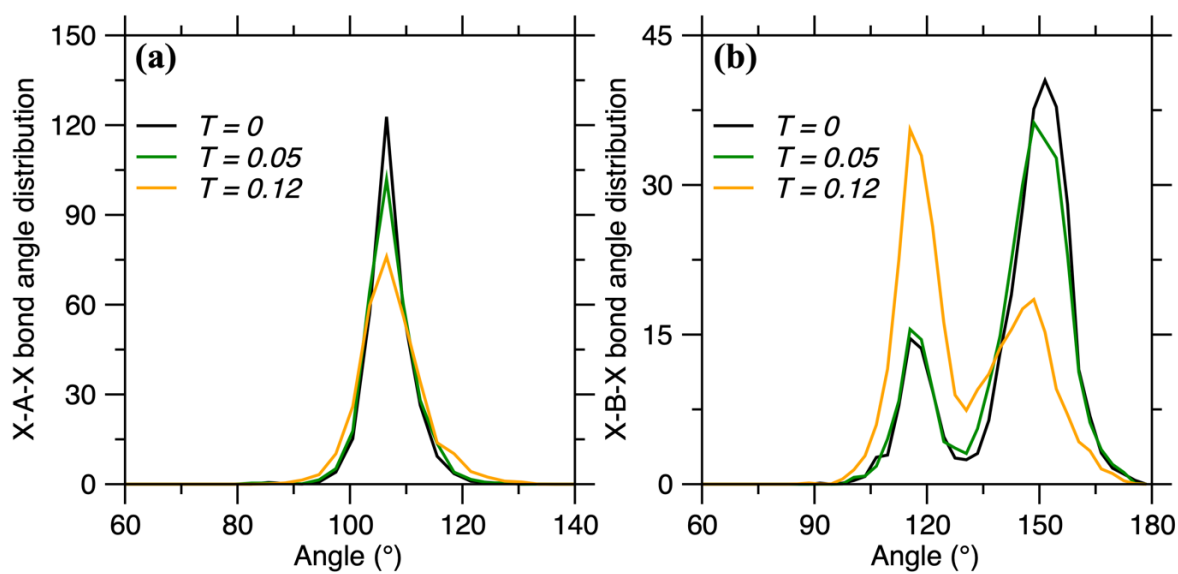


Figure 2-4: Angular distribution of A and B as central atoms respectively at liquidus state ($T= 0.12$), around transition temperature ($T= 0.05$), and glassy state ($T=0$).

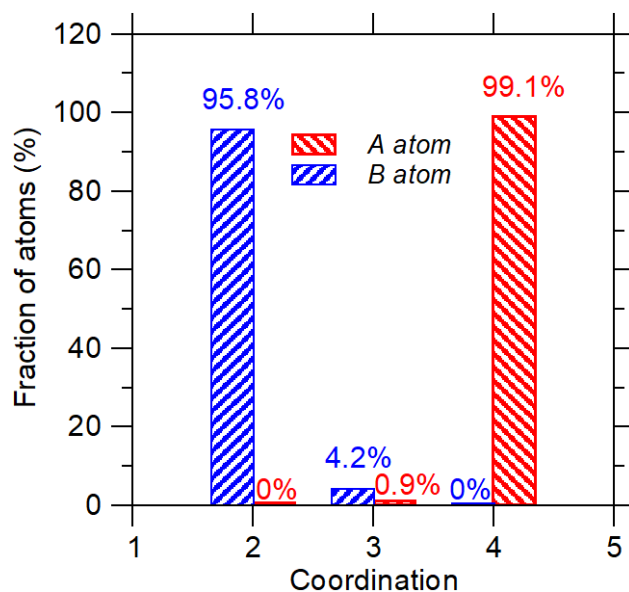


Figure 2-5: Coordination number distribution for A and B atoms at glassy state ($T=0$).

Configurations under different ratios of composition

We continue to extend our system with various connectivity. It should be noted that the volume for each composition is carefully selected to reach a zero-pressure after the melting-quenching, as shown in Table 2-2. Thus, as shown in Figure 2-6, a series of glass structures with various connectivity are simulated. Note that the box size for each configuration is different. As shown in Figure 2-7, the density increases with the ratio of A atom as the volume shrinkages.

Table 2-2: Box lengths of model under different compositional ratios of A atom.

Compositional ratio of A atom	0%	5%	10%	15%	20%	25%	33%
Length of cubic box	75.3576	50.8257	40.8876	35.6013	33.8254	32.2038	30.9978

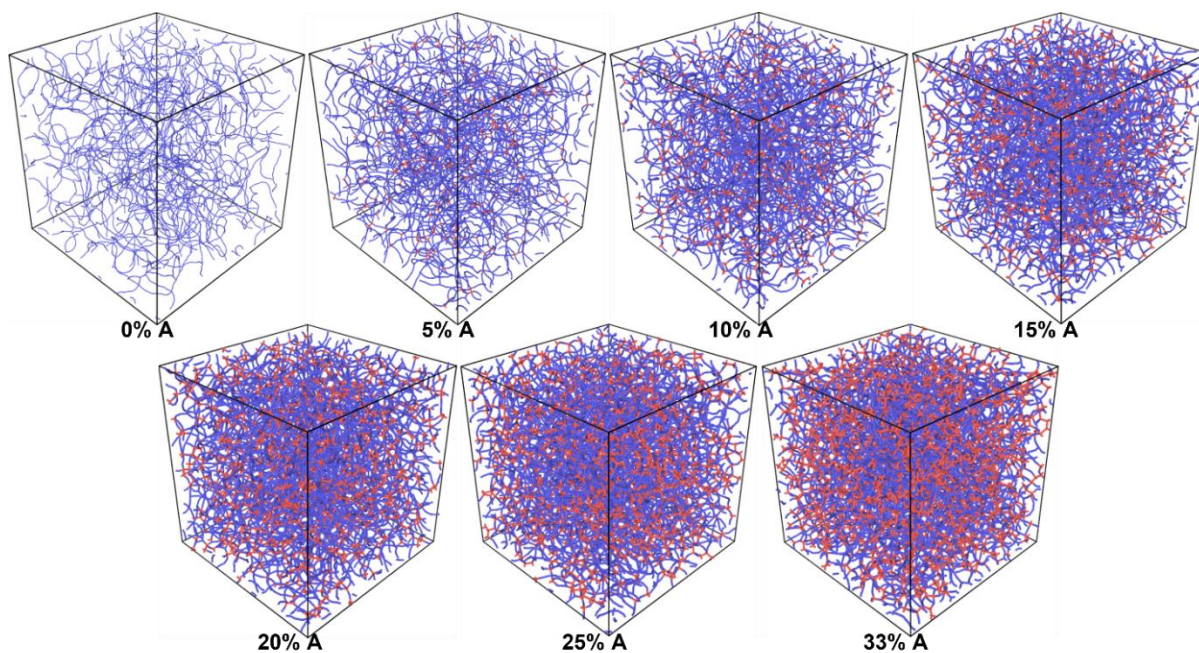


Figure 2-6: Snapshots of $A_xB_{(1-x)}$ as x increases from 0 to 33%. Box sizes are normalized.

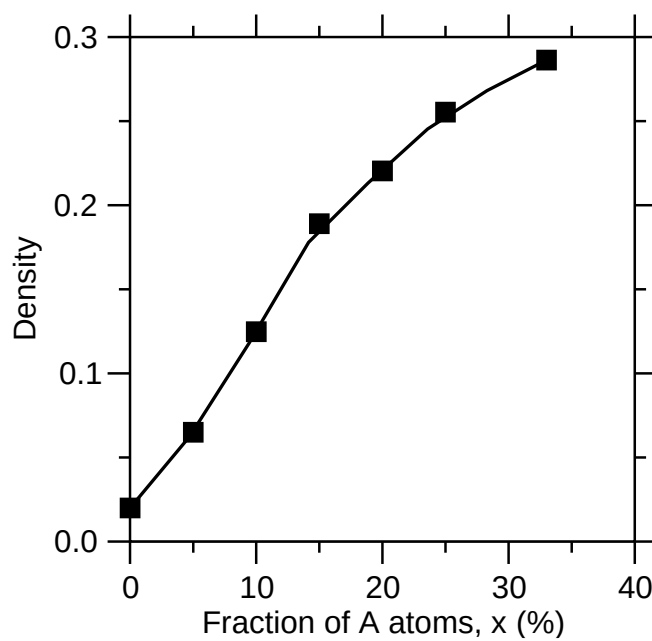


Figure 2-7: Glass densities as the function of the ratio of A atom. The line is to guide the eye.

To investigate the topological features of atomic structure, we analysis the partial PDF and angular distribution of various ratios of compositions. As shown in Figure 2-8, the broadening peak of partial PDF is in line with the fact that more atoms are deviated from their least energy distances with increment of A atom concentration. In addition, the radial bond length change is more significant in A-A and A-B bonds, compared to B-B bonds. This is mainly due to the B-B bonds are more flexible with lower connectivity level and larger angle comparing with A-A and A-B bonds. In Figure 2-9, we observe the angular distribution of X-A-X and X-B-X is broadened and shifted a lower value with the increasing connectivity. It implies that the internal angular deformation is required to fit more AB_2 tetrahedra structures. Both radial and angular distortions indicate an internal stress accumulation with the increasing ratio of A atoms. Again, we examine the CN of A and B atoms separately and collectively for glass under each compositional ratio. In Figure 2-10, the connectivity increment shows a smaller impact on average CN of A atom than B atom. It is easier for B atom with a larger angle and smaller energy penalty compared to A atom, to form a 3-coordinated structure, also aligned with the result in Figure 2-5. The total CN increment is faster than the ideal theoretical trend line, mainly contributed by the growing number of 3-fold coordinated B atoms.

Finally, the model bonding distribution is compared with two amorphous tetrahedral ordering models, random covalent network (RCN) and chemically ordered network (CON) [31-33]. These two simplified network models are often applied to investigate random networks. In RCN, bonds are randomly created without any realistic constraints. However, A-A bonds are prevented when $x < 0.4$ in binary A_xB_{1-x} mixture based on 8-N rule in CON [34]. Figure 2-11 shows the fraction of bonds from our MD simulations is relatively close to the results from RCN, which suggests that

the A-A bonds are not strictly forbidden during the melting-quenching process. Nevertheless, our model yields a higher fraction of the A-A bond compared with RCN when the ratio of the A atom reaches 20%. It should be noted that this difference increases with the ratio of A atom. These results suggest that, rather than randomly located in the box, B atoms are more likely to surround A atom and form A-B bonds. This can be explained by the fact that, when the ratio of A atom increases, the network is dominated by the AB_2 tetrahedra. As a result, the network needs to adjust itself to avoid a mismatch between the cluster formed by A-A bonds and AB_2 tetrahedra to minimize the free energy during the melting-quenching process.

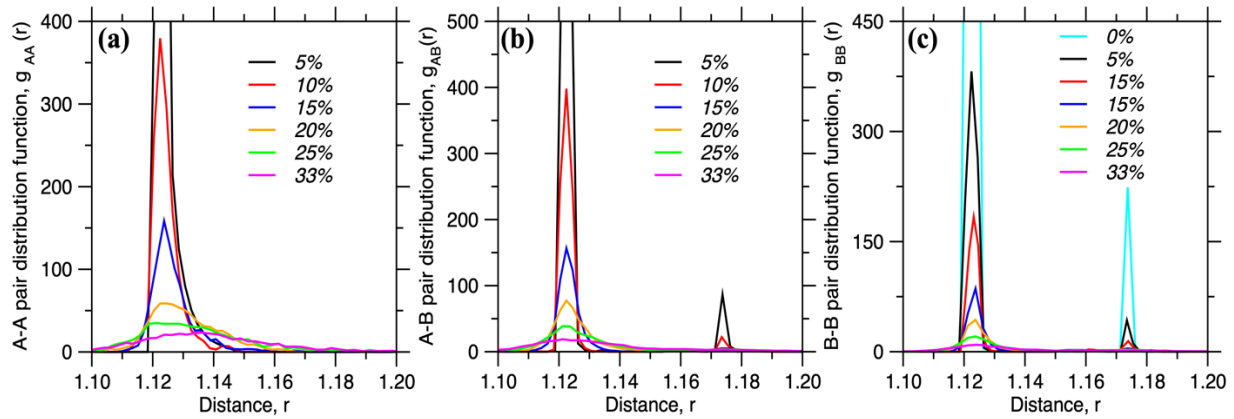


Figure 2-8: Partial PDF between A-A, A-B and B-B atoms, with the ratio of A atom increasing from 0% to 33%.

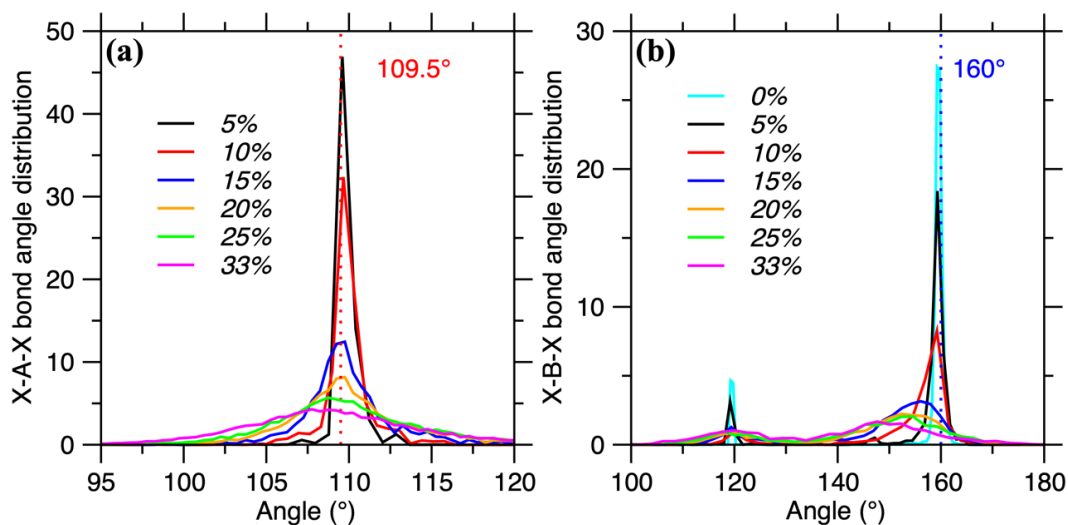


Figure 2-9: Angular distribution of two types of central atom, with the ratio of A atom increasing from 0% to 33%.

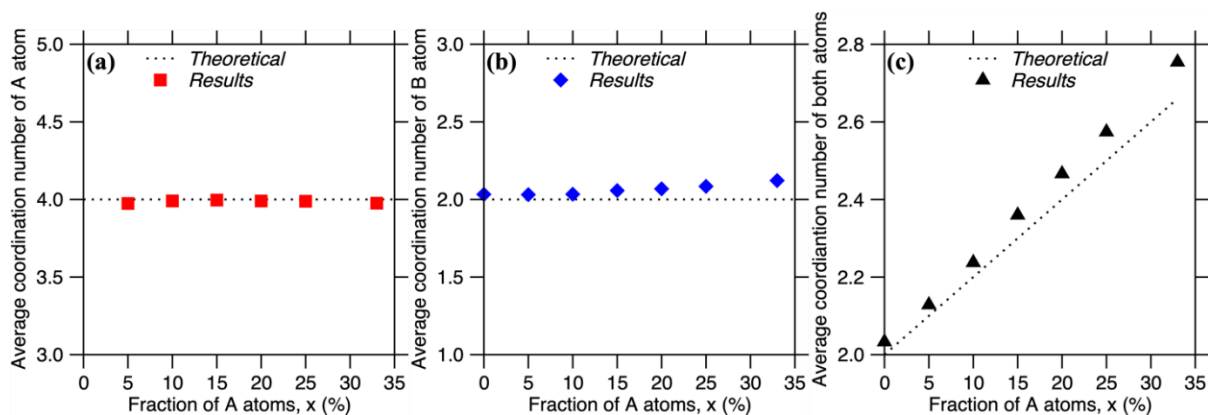


Figure 2-10: Average coordination number (CN) of (a) A atom, (b) B atom, and (c) all atoms, with the ratio of A atom increasing from 0% to 33%.

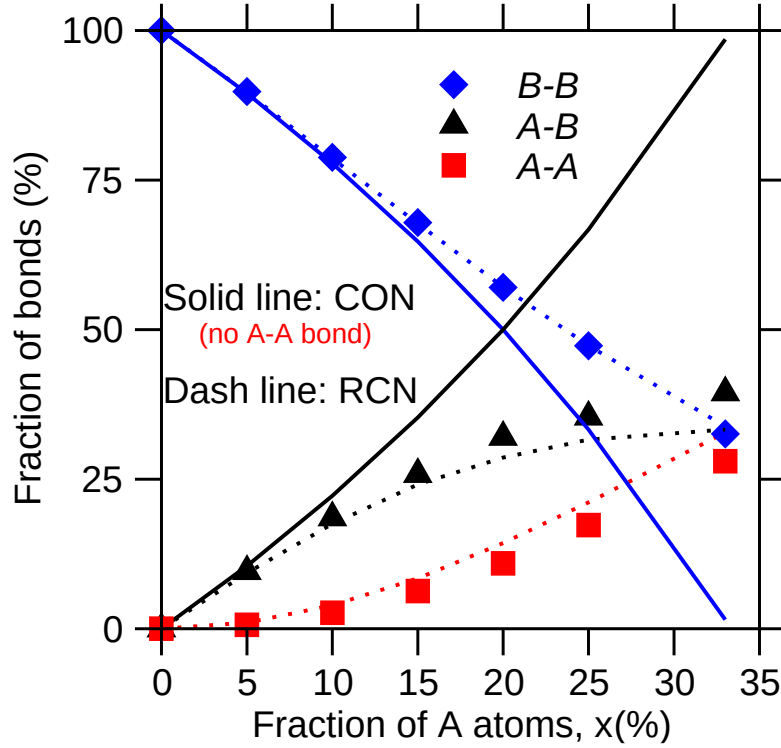


Figure 2-11: Fraction of bonds for A-A, A-B and B-B, with the ratio of A atom increasing from 0% to 33%.

2.4 Conclusions

To conclude, we present a generic modeling of a binary network glass with connectivity tunability. Utilizing a simple interatomic potential to illustrate general network glass behavior, this model provides a more realistic description of network glass compared with classical purely statistical and A-A bond prevention scenario. Following the melting-quenching procedure, we investigate the evolution of structural features and thermodynamic property under different temperatures. The amorphous structure and dynamical arrest suggest the glassy nature of the proposed model. Then we characterize the radial and angular deformation along with the evolution of connectivity, as the function of compositional ratio. The coordination and fraction of

bonds analysis finally endorses the rationality of a 2- and 4- bonded network mixture modeling. After comparing with classical bonding models, our model shows a decent balance between the over simplified models of RCN and CON. Without embedded chemistry, the model shows the ability to capture the effect of connectivity while keeping the simplicity. The generalized parameters can be tuned to isolate the key influential factors in certain physical processes. By combining the topological analysis and machine learning approach, this network glass model can broaden its application to establish the structure-property relationship of binary network system [35-38].

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Chapter 3. Energy landscape signature of flexible to rigid transition in network glass

3.1 Introduction

The out-of-equilibrium feature of glass makes the physics of glass relaxation an open and enduring question [1]. The undesirable structural relaxations can lead to substrate distortion, undermining the stability and performance of glass materials [2, 3]. During the glass rigidity transition, from flexible to stressed-rigid, stability plays a key role in the process of relaxation and is of great importance to understand the nonequilibrium state of glass [4]. From the perspective of energy landscape, the relaxation process is the transition from one local energy minimum to another. The influence of a single change in the local energy landscape can reverberate throughout its neighboring environment, setting off a chain of consecutive relaxations. However, the nonergodic nature of glass relaxation makes it hard to directly observe in the scale of experimental time [5]. Thus, two general types of measurements to study glass relaxation: the rheological properties focusing on viscosity, or the thermodynamic properties mainly based on enthalpy. For MD simulation, enthalpy evaluated by calorimetric method is more accessible by quantifying the residual enthalpy during thermal cycles [6-8]. A stable glass is characterized by a minimized enthalpic difference between both cooling and heating processes, manifesting as hysteresis curves in enthalpy or molar volume changes.

The propensity of glass relaxation during rigidity transition has been explained in the framework of TCT [9-11]. Based on their connectivity, network glasses can be classified as flexible, stressed-rigid, or isostatic, if the number of topological constraints is lower, larger, or equal to the number of atomic degrees of freedom, respectively [12]. Thanks to the absence of any

stoichiometric requirement, the rigidity of glasses can be continuously tuned (e.g., from flexible to stressed–rigid) by changing their chemical composition [13, 14]. Interestingly, optimally-constrained isostatic glasses have been noted to exhibit unusual properties (e.g., nearly-reversible glass transition, low relaxation, desirable mechanical properties, etc.) [15-18]. Especially, the non-aging intermediate state features an almost vanished endotherm between first and second heat scan across glass transition, provides a pathway for phase change material optimization in the application of non-volatile rewriteable media [19]. However, the physical origin of the unusual behaviors and properties of isostatic glasses remain unclear.

To better understand the structural effect on relaxation, Naumis has provided theoretical explanation confirming the relaxation reduction is achieved during rigidity transition, by emphasizing the absence of floppy modes reducing relaxation channels [20, 21]. Later, Bauchy provides a realistic simulation result revealing topological control of relaxation propensity in C-S-H [22]. Meanwhile, the height of energy barrier has been estimated with the means squared displacement (MSD), providing indirect explanations on the role of energy barrier regarding structural relaxation [23]. However, a comprehensive understanding of the relationship between rigidity transition and energy landscape is still lacking.

Here, for the first time, we demonstrate the rigidity transition in the aspect of potential energy landscape. To begin with, we reproduce the phenomena of cycling through the glass transition and get little hysteresis, identifying a region where hysteresis is minimized. We then explore the transition from the structural features of mobility and internal stress. Additionally, we calculate energy barriers and correlate the rigidity transition with the roughness of the energy landscape. We propose that these channels may explain the fragility and ease of glass formation, as multiple

channels make it more challenging for the system to become trapped in a local minimum. Furthermore, a ring analysis reveals relaxation in the medium-range regime across the glass transition, providing additional evidence for the stress-free state. This research significantly contributes to our understanding of rigidity transition and its implications for glassy systems and topology engineering.

3.2 Methods

Thermal cycling methodology

The difference of structural enthalpy before and after relaxation is a direct access to the isostatic state and quantify the residual stress. Experimentally, differential scanning calorimetry (DSC) is a powerful tool due to its high sensitivity, high accuracy, practicality, and direct measurement of thermodynamics [24]. The basic working principle of DSC is to measure the difference amount of heat flow to increase the sample and reference temperature are monitored as a function of time and temperature. During a specific heat path, either cooling or heating, the absorbed or released heat will be measured by the calorimeter. In simulation, the cooling and reheating process could reveal the enthalpic gap of relaxation, which indicates stress.

The system under investigation is composed of 3200 atoms with normalized Stillinger Weber potential. All the systems are performed numerical cooling-reheating cycles across the glass transition in NVT ensembles and zero pressures. Starting from an equilibrated liquidus state at the temperature of 0.1, configurations are then cooled to 0 at different rates from 0.05 to 50. Once reaches the glassy state, the systems are subsequently reheated back to the initial temperature at the same rate. To exclude thermal fluctuation, the values of ground -state

enthalpies are collected with the temperature. To account for any potential randomness in the system, the entire cooling-reheating process was repeated on five independent configurations, all with the same compositional ratio. This approach allowed us to mitigate any biases resulting from variations in the initial configurations, ensuring a robust and statistically significant analysis.

Mean square displacement (MSD)

To evaluate the flexibility of the system, the mean square displacement (MSD) is adopted to compute the atomic mobility [25]. The displacement of each atom is tracked after applying an energy bump to activate atomic motions. To avoid glass transition, the elevated temperature, bestowing the energy bump, is selected based on the fictive temperature of each configuration.

Stress per atom

To determine the degree of stress acting in the atomic network, we adopt the concept of “stress per atom.” Although stress is ill-defined at the atomic level, we rely here on the formalism proposed by Thompson, which expresses the contribution of each atom to the virial of the system [26]. It is important to take Voronoi volume into consideration since our system volume is different [27].

Energy barrier

Activation-relaxation technique nouveau (ARTn) is adopted here to compute the energy barrier (Eb) by identifying the saddle point of the energy landscape [28-30]. The energy barrier, namely corresponds to each atom, is yielding from its neighboring environment. By randomly applying

perturbations on central atom and its neighbors, the displacement drives the starting local minimum in energy landscape to move towards the direction of the first-order saddle point, until it reaches a new minimum. The local deformation radius is chosen as being equal to the cutoff radius used for the calculation of the non-affine displacements. 20 saddle point searching events are performed for each atom, which is proved to be large enough to converge to a local minimum [31]. In our case, we choose the smallest E_b value out of the 20 events to represent the minimum local energy barrier. Thus, each atom corresponds to one value of the energy barrier E_b .

Ring

To study the medium range order of glass structure, the closed loop chain of atoms is defined as ring. In 1967, King gives the first definition of ring relying on the rule that a ring is linked by shortest paths between two of the nearest neighbors of a given node [32, 33]. Later, in 1990, Guttman proposed another criterion for ring definition in silica material, which only counts the Si atom as the nodes of ring and define a ring is the shortest path that comes back to a given node starting from one of its nearest-neighbor Si atoms [34]. Guttman's criterion is the subset of King's criterion, and it reduces the number and the size of the ring statistics. In our case, we adopt Guttman's criterion where the 4-bonded B atom is the given node. Thus, the smallest ring size would be 3.

3.3 Results and Discussion

Features of glass transition

To establish our conclusions, we utilize our previously proposed random 2- and 4-fold model as the study system. The AB mixture composed of AB_{4/2} tetrahedra is investigated by Molecular Dynamics (MD) simulations in NVT ensemble. To provide an initial visualization of the glass's behavior, snapshots of flexible, isostatic, and stressed-rigid glasses are present in Figure 3-1(a). It vividly illustrates the distinct differences of bond numbers among the configurations, reflecting the various levels of connectivity. To quantify connectivity, we employed the concept of the number of constraints (nc) based on topologically constrained theory (TCT). The number of constraints (nc) for whole configuration is defined as $nc = 2.5 \cdot CN - 3$, where CN represents the glass average coordination number [12]. Figure 3-1(b) illustrates the relationship between the connectivity (nc) and the average coordination number, revealing a linear incremental trend as a function of composition, serving as a basis for our next investigations. In the subsequent sections, we delve into the glass and rigidity transitions, exploring how changes in connectivity impact the properties and behaviors on the glassy structure, dynamics, and thermodynamic properties, deepen our understanding of the glass transition and relaxation.

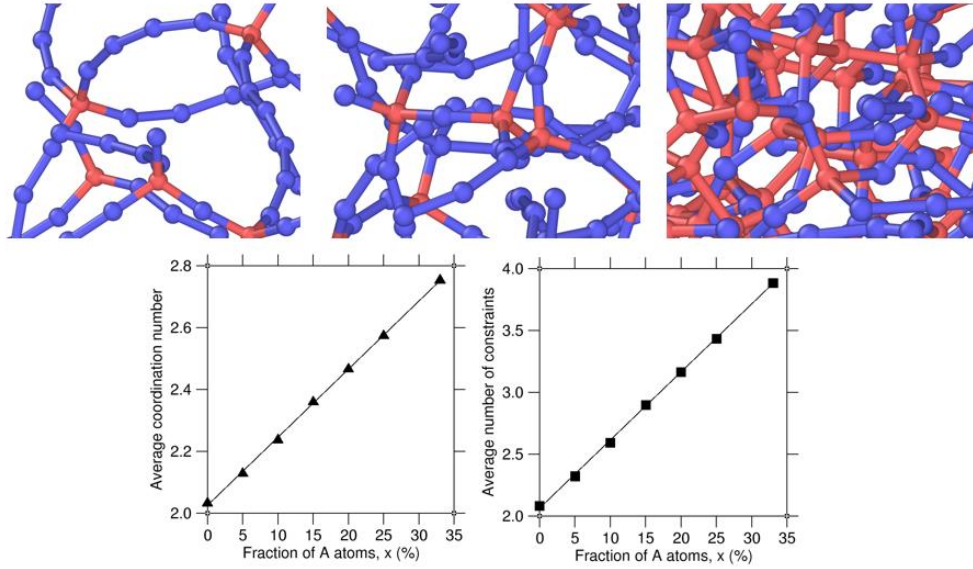


Figure 3-1: Structure of flexible, intermediate, and stressed-rigid glass. (a)-(c) Snapshot of flexible, intermediate, and stressed-rigid glass. The structure is composed of 4-bonded A (red) atom and 2-bonded B (blue) atom. The level of connectivity is increasing from the flexible to stressed-rigid structure. (d) Average coordination number (CN) of all atoms, (e) Average number of constraints (nc), with the fraction of A atom.

To quantify the glass relaxation, systematic isochoric cooling/heating cycles were performed across the glass transition. Figure 3-2(a) shows a hysteretic behavior of enthalpy for flexible, isostatic and stressed-rigid structures. The enthalpy cooling curve is always higher than the reheating curve at same temperature since the residual internal stress has not been fully relaxed during cooling process. The figure shows glass fictive temperature is around $T = 0.6$, where we should focus on comparing the cooling/reheating gap, though is slightly different under various rigidity. This observation can be explained by the fact that relaxation can only occur around $T = T_f$, where the relaxation time becomes comparable to the typical observation time. When temperature is much larger than T_f , the relaxation time is several orders of magnitude lower than

the simulation time (picoseconds) and cannot be observed. On the other hand, at temperature much lower T_f , the large viscosity makes the atomic dynamics too slow, and the relaxation is kinetically frozen [6]. Notably, the isostatic glass exhibits a significantly smaller gap between the enthalpic curves of cooling and heating compared to the flexible and stressed-rigid cases. The difference characterizes the ground-state enthalpy relaxation, which is then defined as $\Delta H = H(\text{cooling}) - H(\text{heating})$. ΔH reaches the maximum at the vicinity of glass transition, where close to the fictive temperature, as shown in Figure 3-2(b).

The simulations reproduce the phenomenology of H_{max} reaches minimum around fictive temperature. The relaxation dynamics can be further fitted with a Gaussian function:

$$\Delta H = H_{max} \exp \left[\frac{-(T - T_{max})^2}{2\Delta T^2} \right]$$

where H_{max} is the maximum extent of enthalpy change, T_{max} is the temperature corresponding with H_{max} , ΔT is the temperature range of the relaxation. Note that Gaussian fit might not be a perfect fit for relaxation since ΔH is not symmetric. The goal of the fitting is to extract the three fitting parameters, which can provide relative thermodynamic information for all the configurations.

As shown in Figure 3-2(c), a minimum region can be thus defined after averaging maximum values of ΔH , indicating a near-zero enthalpic change can be achieved around stress-free region. Note that the intermediate region is designated to guide the eye, not strictly defined between 2.7 and 3. These results provide valuable insights into the glass relaxation dynamics and the relationship between ΔH and the glass transition temperature. The ground-state enthalpy

relaxation, as measured through these cooling and heating cycles, serves as a crucial parameter to further our understanding of the thermodynamic behavior of glassy materials.

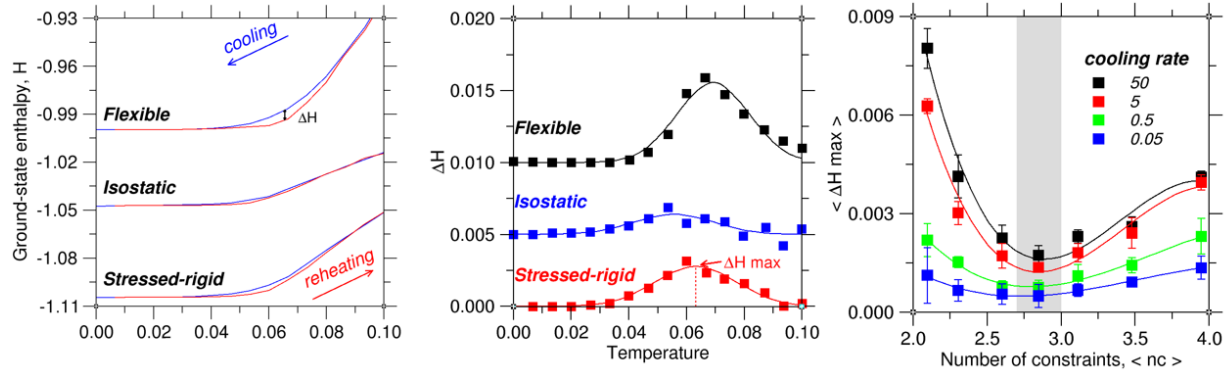


Figure 3-2: (a) Evolution of ground-state enthalpy as the function of temperature for flexible, isostatic and stressed-rigid glass in NVT ensemble under the cooling rate of 0.5. The blue and red curves refer to the cooling and re-heating process, respectively. (b) Relaxation enthalpy, ΔH , (i.e., difference of ground-state enthalpy upon cooling and reheating) as a function of temperature. (c) Maximum of ΔH as the function of number of constraints under different cooling rates.

Structural features (MSD and Stress)

To gain a deeper understanding of the transition region, we conducted an analysis of the internal mobility across different phases. The average square root of the Mean Square Displacement (MSD) of A and B atoms was used as an indicator of the transition from the flexible phase towards the intermediate phase. Figure 3-3(a) presents the computed MSD as a function of the average number of constraints ($\langle nc \rangle$). In the rigid region where $\langle nc \rangle$ is larger than 3, we

observed only a small change in MSD. This phenomenon can be explained by the high rigidity present in this region, which effectively restricts the motion of atoms and leads to limited internal mobility. Conversely, in the region where $\langle nc \rangle$ is smaller than 3, the MSD exhibits a sudden slope increment. This increase in MSD signifies a higher internal mobility in the flexible structure. The presence of fewer constraints allows atoms to move more freely, leading to an enhanced level of internal motion.

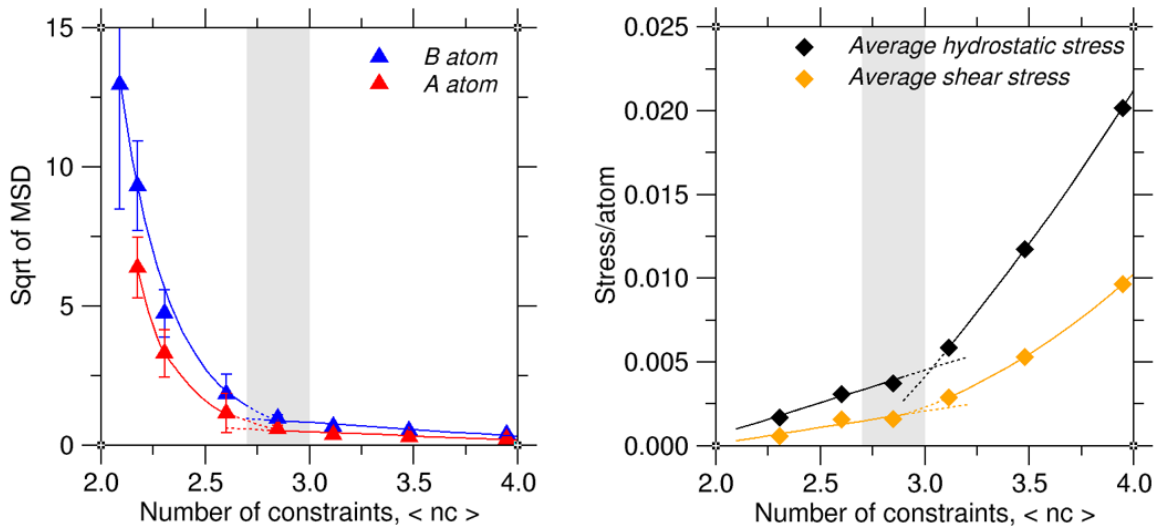


Figure 3-3: (a) Square root of MSD, (b) stress/atom as the function of number of constraints ($\langle nc \rangle$).

The internal stress within the network provides another insightful perspective for directly assessing the atomic features. Figure 3-3(b) illustrates the average hydrostatic and shear stress per atom as a function of the average number of constraints ($\langle nc \rangle$). Similarly, as $\langle nc \rangle$ surpasses the intermediate region, a sudden increase in the slope is observed. This observation aligns with previous reported experiments and simulations, further corroborating the significance of this transition. In the flexible-intermediate regime, the connectivity increment does not appear

to play a crucial role in internal stress accumulation. This is due to high floppiness within the system, which effectively counterbalances the stress. However, in the transition from the intermediate to stress-rigid phase, the increasing number of constraints becomes mutually dependent with tension or compression, resulting in an unbalance that leads to internal stress accumulation.

Interestingly, the mobility, as measured by MSD, does not exhibit significant changes as the number of constraints increases beyond the intermediate region. Therefore, the transition from flexible to isostatic is primarily governed by atomic mobility or MSD, as the relative floppy structure provides more space for the motion of atoms. Conversely, stress accumulation is not prominent in the flexible region, suggesting that the isostatic to stressed-rigid transition is predominantly contributed by the stress increment.

By analyzing the internal stress and its relationship with atomic mobility, we gain a comprehensive understanding of the transitions between different phases. The interplay between stress and mobility serves as a critical factor in determining the rigidity and structural stability of the system. These findings offer valuable insights into the mechanisms governing the transitions from flexible to intermediate and from isostatic to stress-rigid, further enhancing our understanding of the glass transition and the underlying physics of glassy materials.

Energy landscape signature for flexible-rigid transition

Having established the phenomenology of the ground-state enthalpy minimum, atomic mobility, and internal stress, we now delve into a more fundamental physical origin of the rigidity transition, focusing on the potential energy landscape. To accomplish this, we calculate the

height of energy barriers (E_b) using the ARTn algorithm. It is essential to consider that all configurations have different volumes, and the computation of energy barriers relies heavily on the eigenvalue threshold. To ensure accuracy, we conducted a thorough search to identify the minimum energy barrier for all glasses pertaining to each atom. This meticulous approach guarantees that we obtain reliable and meaningful results concerning the energy landscape and its impact on the rigidity transition. Figure 3-4 presents the distribution of energy barriers for each atom across all configurations with varying numbers of constraints ($\langle nc \rangle$). Remarkably, we observe that the height of the energy barriers (E_b) reaches its maximum in the region of the intermediate phase, while it diminishes in both the flexible and stressed-rigid phases. The presence of the highest energy barrier in the intermediate phase suggests that the atoms in this configuration are more stable with larger confinements, resulting in reduced glass relaxation and enhanced rigidity.

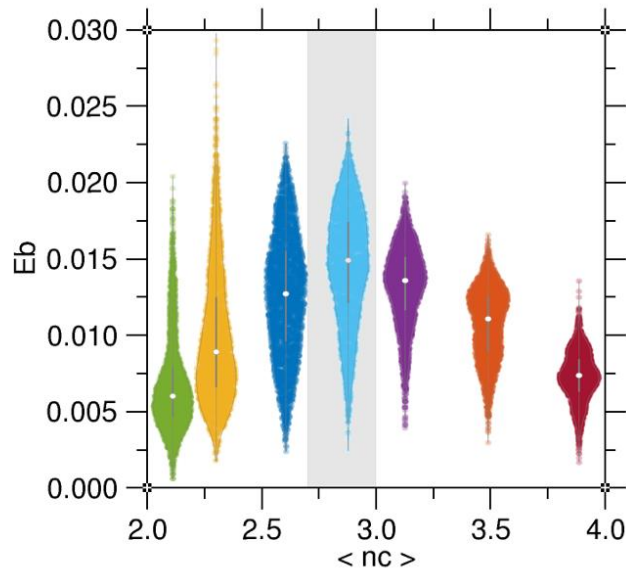


Figure 3-4: Energy barrier distribution for various number of constraints, $\langle nc \rangle$.

By exploring the energy barriers and their distribution across different phases, we gain critical insights into the underlying physics governing the rigidity transition. The connection between energy barriers and the stability of glassy configurations sheds light on the intricacies of the potential energy landscape and its role in dictating the behavior and properties of glassy materials. These findings contribute to a deeper understanding of the fundamental mechanisms driving the glass transition and the transition from flexible to isostatic and stress-rigid phases.

Ring analysis

Having explored the short-range atomic structure, our focus now shifts to investigating the medium-range regime. In this study, by employing Guttman's ring criteria, that define the 4-bonded B atom count as the node, we define the threshold as six for dividing small or large rings. Previous studies have shown that the six-membered ring appears stress-free in silica, and the threshold is also validated in our model [35]. The ring number distribution for all the glasses from $\langle n_c \rangle$ equal to 2.3 to 3.95, is calculated as illustrated in Figure 3-5(a). The total number of rings are small for floppier structures as they contain less 4-bonded B atoms. In the figure, rings that are larger than 18 can be ignored as the large size ring is too floppy to be considered. Notably, the distribution peaks exhibit a clear shift towards smaller ring sizes as $\langle n_c \rangle$ increases. It is known that smaller-size rings are energetically unstable with larger internal stress. The distribution shows glass with larger $\langle n_c \rangle$ is dominated by small-size rings, which exhibits significantly internal stress, and the result aligns with the plot of stress/atom mentioned earlier.

To have a closer look into how the network relaxation is facilitated by ring size, we performed a comparison before and after a glass relaxation. To ensure the rings are only perturbed and

relaxed locally instead of fully reconstructed, we heat the glass at the temperature of 0.02, much lower than the transition temperature while still providing enough energy for relaxation. The configuration is kept for a long time to ensure sufficient network reset and we can then compare the configurational change before and after relaxation.

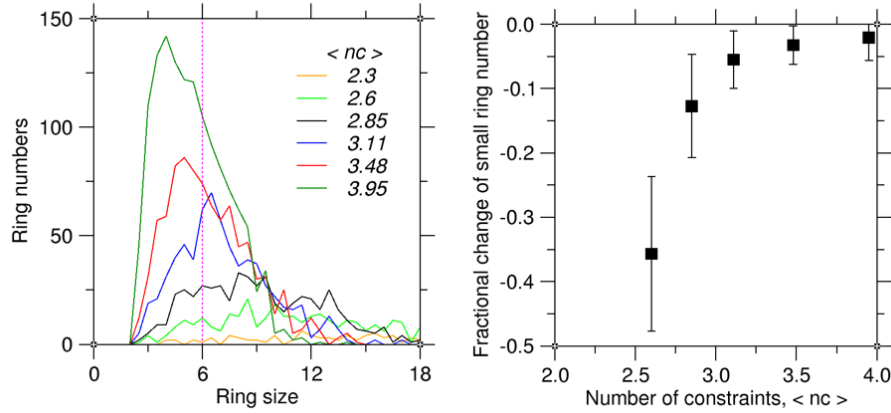


Figure 3-5: (a) Ring distribution, the purple line marked where the ring size equal to 6. (b) Fractional change of small-size ring (<6) population before and after glass relaxation.

To approach the medium-range mechanism for relaxation, for now, we only focus on small-size rings that have less than six members. Figure 5(b) shows overall the population of small-size ring decreases as the fractional change is negative, indicates the relaxation reduces the fraction of small-size ring. This is within expectation as the internal force is relaxed by breaking the small-size ring and reconstructing larger-size rings. As the global nc increases, from flexible to stressed-rigid, the fractional change becomes smaller, indicates the relaxation in floppier network is achieved by reducing the number of small-size rings. However, in the stressed-rigid region, glasses are mainly dominated by small-sized rings, the relaxation does not decrease their

fractional populations. To overcome this limitation, we further monitor how the size of small rings are changing in the process of stress releasing.

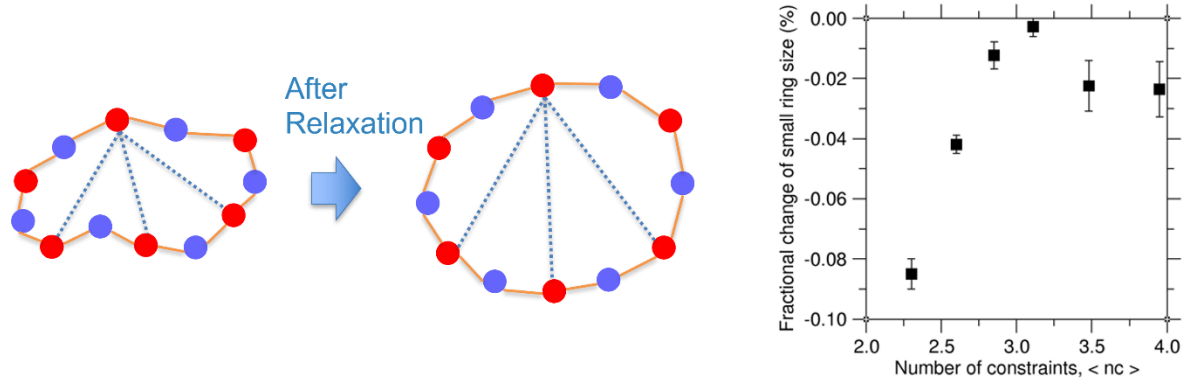


Figure 3-6: (a) Schematic of defining the size of change before and after relaxation. (b) Fractional change of small ring size as the function of number of constraints ($\langle nc \rangle$).

To investigate the relaxation process, we performed a comparative analysis between different configurations, where one configuration is further relaxed compared to the initial configuration. Figure 3-5(b) illustrates the fractional change, which is obtained by subtracting the small ring population of the more relaxed glass from that of the initial glass. A negative fractional value indicates a reduction in the population of small rings after further relaxation, signifying that relaxation is achieved by breaking more stressed rings. This transition from flexible to less floppy is facilitated by the reduction of small ring structures. However, in Figure 3-5(a), it becomes challenging to distinguish the reduction in small ring population in configurations with larger numbers of constraints ($\langle nc \rangle$). This difficulty arises due to the significantly dominant portion of small rings in glasses with higher nc values.

Therefore, to further illustrate the effect of relaxation in the medium-range order, we introduce the concept of size deformation. The size of ring can be reflected by the distances inside the ring, and we thus define the ring size by summing the distance between all the 4-bonded atoms, as illustrated in Figure 3-6(a). As shown in Figure 3-6(b), a negative value in size deformation indicates a reduction in size after relaxation. Notably, the size deformation approaches almost zero near the stress-free region and coincides with the isostatic state. It means glass relaxation not only appears in the way of reducing small rings number, but also expands the size of rings without breaking. When the transition shifts from isostatic to stressed-rigid, the relaxed rings appear larger than the initials. This phenomenon can be attributed to the internal stress-driven size shrinkage, where stressed-rigid configurations experience greater deformations due to the build-up of internal stress. By analyzing the fractional changes in small ring population and size deformation, we gain insights into the relaxation process in the medium-range order. The small-size rings, where internal stress is accumulated in, serve as the signature for stress releasing structural relaxation. These findings provide valuable information on the structural changes occurring during relaxation and their connection to the stress-driven and floppy-to-rigid transitions. The interplay between ring structures, size deformation, and stress accumulation offers deeper insights into the mechanisms governing the glass transition and the stability of glassy materials.

Relaxation

To better understand the results mentioned earlier, the relaxation process for structure with different rigidity has been shown in Figure 3-7. For flexible state, it takes a small energy to overcome the barrier to relax to a new minimum layout due to the loose connection, also proved in MSD results, and it thus corresponds to a small E_b [36]. For isostatic state, the extra connection compared with the flexible structure makes it harder to break the initial equilibrium, and the E_b value becomes larger. This is supported by the results of E_b distribution. For stressed-rigid state, the redundant constraint does not further increase the height of energy barrier to leave the initial state but lifts the initial state energy and induces the instability of the network. This extra internal stress acts as a driving force that assists the structure to leave the current minimum basin, and thus increases the propensity of structural relaxation [22]. Consequently, a similar lower level of E_b is observed in stress-rigid and flexible state, compared with isostatic state, with different mechanisms behind.

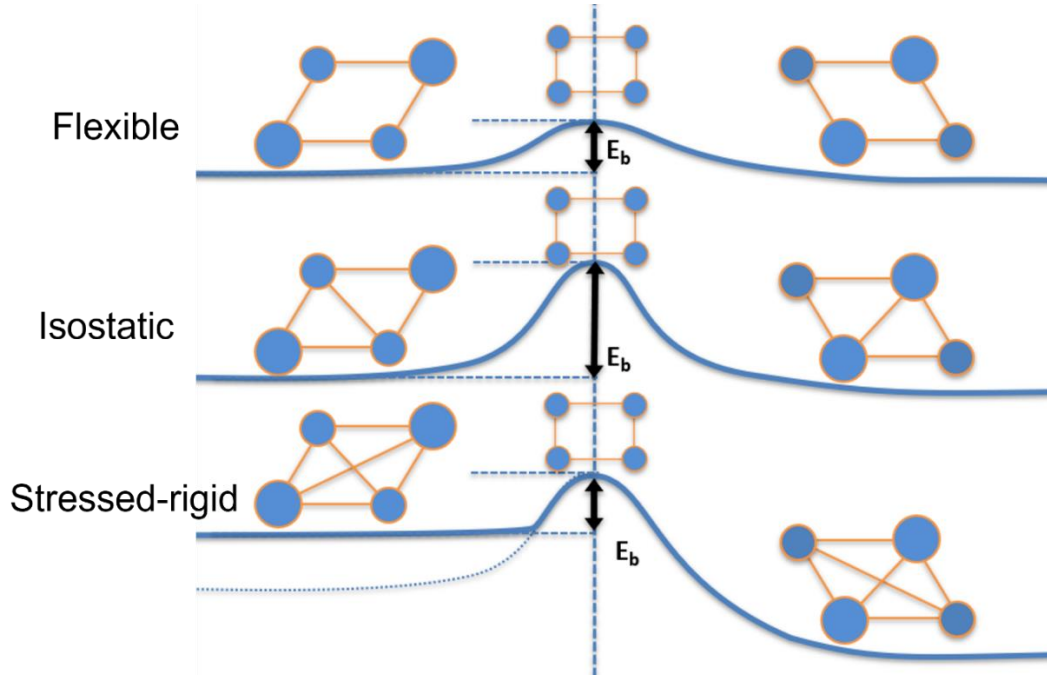


Figure 3-7: Schematics of the relaxation process with initial and final state for flexible, isostatic and stressed-rigid atomic network. The corresponding height of energy barrier is denoted by E_b . Network reset at the saddle point is shown in the middle. For stressed-rigid network, the dash line is hypothetical energy level without the extra constraint.

Heterogeneity

Previous results and discussion have come to a comprehensive conclusion in the aspect of energy landscape for glass relaxation during rigidity transition. However, two more things need to be clarified. (i) Region for isostatic state, need additional information to prove region instead of a single threshold. (ii) The volume effect needs to be excluded since the glasses with various connectivity are greatly differ in volume. The glass with global $\langle n_c \rangle = 2.85$ is selected to be diced into $6 \times 6 \times 6$ small cubes, then we will have 216 small configurations with different local $\langle n_c \rangle$ values. Similar with the global $\langle n_c \rangle$, the local $\langle n_c \rangle$ values are also averaged over all the

atoms inside one single cube. Figure 3-8 shows how the 3400-atom glass is split into small cubes and each cube contains about 16 atoms. In this case, each cube would correspond to one local $\langle nc \rangle$ value. Similarly, the cubic local value for ΔH , MSD, stress/atom and E_b is obtained by averaging over number of the cubic atoms. As shown in Figure 3-9, by fitting the curve of ΔH as the function of temperature, $\Delta H_{\max}$ can be gained for each cube. Thus, the maximum enthalpy difference curve can be plotted, revealing a reversibility window with abrupt change at the transition edges. Note that comparing with the whole configuration results, which only defines a minimum region of $\Delta H_{\max}$, the reversibility window is clearly displayed.

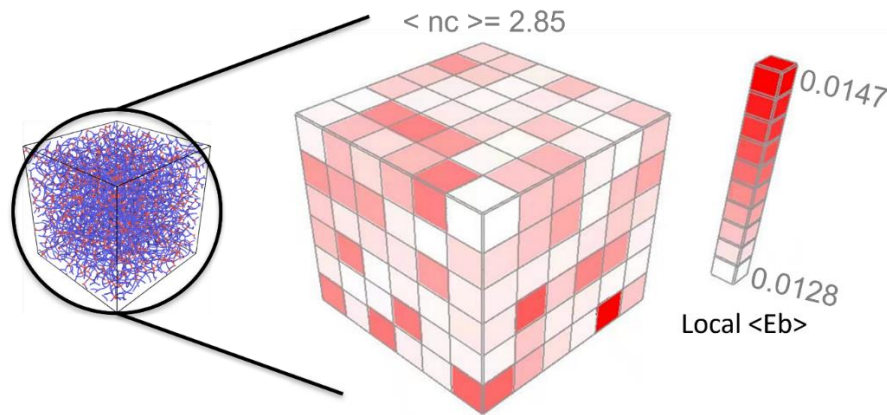


Figure 3-8: Schematic of how the glass structure is split into small cubes. Take E_b value as an example, the color intensity represents the E_b level for each cube.

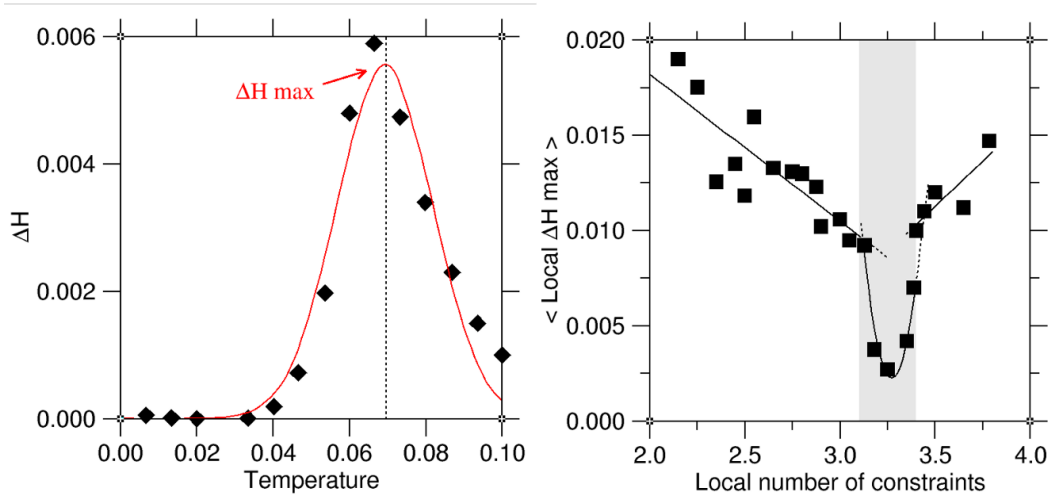


Figure 3-9: (a) Relaxation enthalpy, ΔH , (i.e., difference of ground-state enthalpy upon cooling and reheating) as a function of temperature. The Gaussian fitting provides the value of ΔH_{max} . (b) Maximum of ΔH as the function of number of constraints under the cooling rate of 0.5.

As shown in Figure 3-10(a-c), the local MSD, stress/atom, and E_b shows similar trend as our previous results. Note that the width and the center of the reversibility window is just to guide the eye. The amount sudden decrease of thermally reversibility window could be by an order of magnitude [13]. When changing the dicing strategy to more or less cubes, the trend of results are similar. As mentioned earlier, the correlations between n_c vs. E_b has been demonstrated to the short-range order effect to the energy landscape. In order to discover the medium-range order contribution to energy landscape, the local E_b as the function of local ring size is plotted. In Figure 3-10(d), local E_b appears a maximum where ring size equal to six, indicating the medium-range structure also plays a role in governing energy landscape as the six-membered ring presents stress-free.

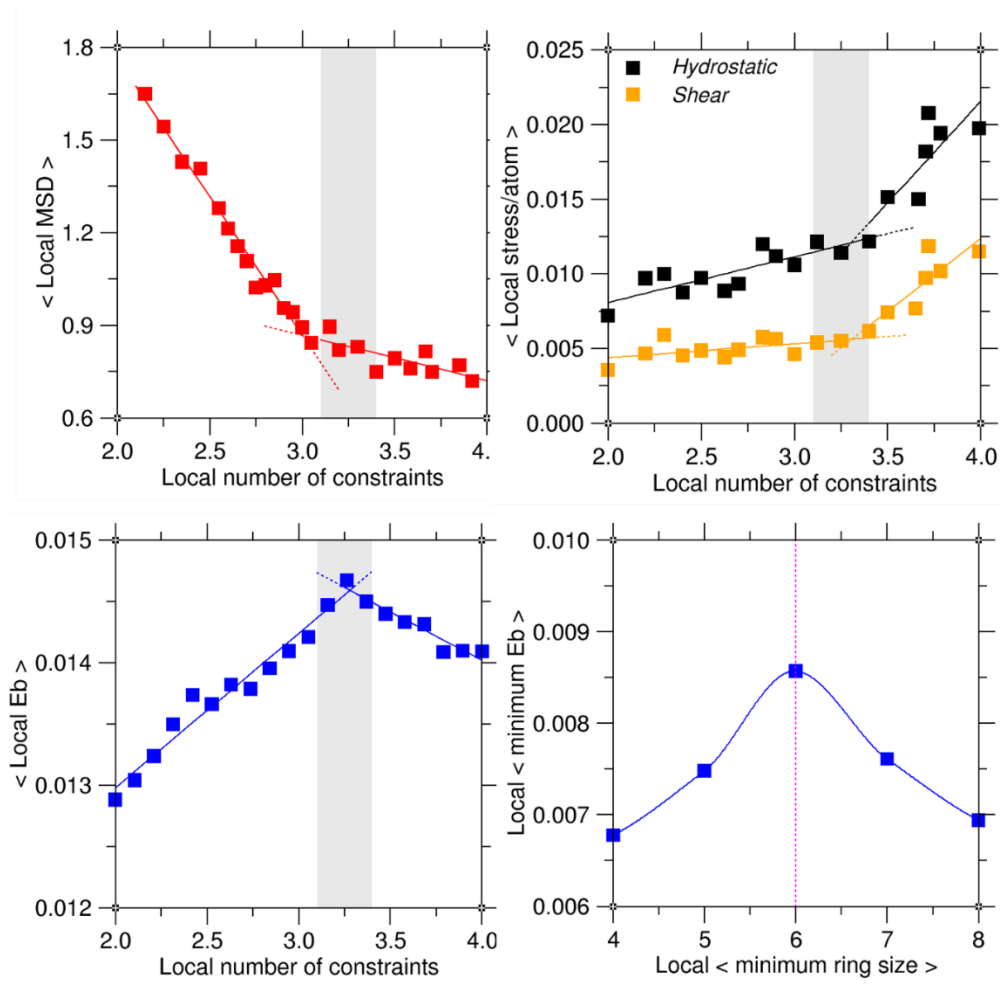


Figure 3-10: (a) Local MSD, (b) local hydrostatic and shear stress, (c) local Eb as the function of local number of constraints. (d) Local Eb as the function of Local ring size.

3.4 Conclusions

Generic network glasses with various rigidity are studied under cooling/reheating thermal cycles, mimicking DSC experimental process to quantify the residual stress. The result of enthalpic hysteresis shows the flexible to stressed-rigid structural transition, highlighting the isostatic state where the enthalpic difference reaches minimum. Along with the structural signatures of MSD and stress/atom further explain the main factor to the region of flexible and stressed-rigid. The

network with high mobility mainly causes the flexible state while the stressed-rigid state is governed by the redundant internal stress. To better understand the physical origin of isostatic state, the height of barrier calculated by ARTn appears a maximum at isostatic state. The larger confinement of high energy barrier ensures the higher stability of the isostatic state, compared to flexible and stressed-rigid states. All the energy landscape signatures have been investigated and aligned with the isostatic state.

To decode the medium-range effect on glass relaxation, our observation on ring size is consistent with previous studies on the 2-fold and 4-fold mixture, where it was found that the minimum stress occurs when the ring size is 6. As the ring size decreases from 6, stress accumulates, while an increase in ring size results in a floppier structure. The portion of small rings within each glass configuration represents its medium-range feature. Analyzing the distribution of small rings allows us to gain insights into the medium-range structural characteristics of the system under varying constraints. By combining the information from the stress/atom results and the ring number distribution, we establish a connection between the ring size and the stress accumulation. This correlation contributes to our understanding of the medium-range regime and how it affects the overall rigidity and stability of the glassy configurations. Additionally, it sheds light on the role of ring structures in influencing the properties and behaviors of glassy materials.

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Chapter 4. Unveiling the effect of fragility with simple and realistic models

4.1 Introduction

Chalcogenide glasses serve as phase change materials (PCMs) are ideal candidates for rewritable data memory medium due to their special properties between amorphous and crystalline phases, such as rapid and reversible transformation, high contrast in conductivity and reflectivity [1]. To better understand the chalcogenide glass, previous studies heavily rely on the ab initio simulation [2-4]. As its density function is based quantum chemistry, the computation cost is huge and only a small configuration can be calculated. The development of reliable, yet computationally efficient empirical interatomic forcefields is key to facilitate the modeling of glasses. However, to date, no robust empirical potential is available for chalcogenide glasses. This arises from the fact that such glasses exhibit various difficulties, e.g., strongly directional covalent bonds, combination of homopolar and heteropolar bonds, and varying coordination numbers [5]. Here, we adopt our recently proposed machine-learning-based optimization scheme [6-8] to parameterize an empirical interatomic potential for Ge–Se chalcogenide glasses, wherein the forcefield parameters are optimized to ensure a good match with ab initio simulation data. We demonstrate that our new interatomic forcefield yields a level of accuracy that is comparable to that offered by ab initio simulations while being several million times more computationally efficient. This enables for the first time the simulation of large, slowly-quenched Ge–Se glasses, which reveals new insights into their atomic structure.

To study the chemistry effect of the empirical $\text{Ge}_x\text{Se}_{1-x}$ potential, we adopt a comparison with the previously mentioned generic model. As they are all based on the SW potential, the extra

parameterization of the empirical $\text{Ge}_x\text{Se}_{1-x}$ potential acts as the realistic chemistry effect comparing with the generic network glass. Thus, by comparing the thermodynamic features, we can illustrate the difference of the thermal reversibility window. The shape of the enthalpic difference indicates that the chemistry effect plays a critical role on increasing the internal stress when the transition shift from isostatic to stressed-rigid, since the sudden increase of ΔH_{max} is more predominate than in generic model. In glass physics, fragility characterizes how rapidly the dynamics of the supercooled liquid slow down as it is cooled toward the glass transition [9]. Glass fragility can be gained by fitting the enthalpic curve by Gaussian fitting and it is directly reflected by the range of glass transition temperature [10, 11]. As a result, a fragility window is observed as the function of composition, coincident with the reversibility window. The fragility trend shows a well alignment with experimental results, highlight the ability of the empirical forcefield revealing the rheological properties of $\text{Ge}_x\text{Se}_{1-x}$ glass.

4.2 Method

The molecular dynamics simulations were conducted using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) developed by Sandia National Laboratories [12]. Simulations on four compositions $\text{Ge}_x\text{Se}_{1-x}$ have been performed at constant volume on systems consisting of 8000 atoms. In this study, the interatomic potential parameterized is Stillinger-Weber (SW) potential described as follows:

$$U(r_{ij}, r_{ik}, \theta_{ijk}) = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) \quad \text{Eq. (1)}$$

$$\phi_2(r_{ij}) = A_{ij} \epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp \left(\frac{\sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \quad \text{Eq. (2)}$$

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \left[\lambda_{ijk} \epsilon_{ijk} (\cos \theta_{ijk} - \cos \theta_{0ijk})^2 + \beta_{ijk} \right] \exp \left(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \exp \left(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}} \right) \quad \text{Eq. (3)}$$

where the subscripts ij , ik , and jik represent pairs and triplets involving atoms i , j , and k , correspondingly. ϵ and σ are the energy and distance scaling parameters, respectively. A , B , p , q , λ and γ are fitting parameters for 2-body and 3-body interatomic distances and angles. The 3-body angular term attains tetrahedral geometry [13]. Note that a repulsive force term β_{ijk} is added to Eq. (3) for the conventional SW potential, helps to keep 2-bonded and 4-bonded structure and avoid local atomic phase separation.

To optimize the forcefield, a cost function needs to be defined and the optimization is based on it. In this study, to parameterize the potential of $\text{Ge}_x\text{Se}_{1-x}$ glass, the difference between partial pair distribution function (PDF) $g(r)$ from empirical MD and ab initio molecular dynamics (AIMD) simulations is used. The difference can be defined as an R_χ ,

$$R_\chi = 100\% \cdot \sqrt{\frac{\sum [g^{AIMD}(r) - g^{MD}(r)]^2}{\sum [g^{AIMD}(r)]^2}}$$

The optimal sets of forcefield parameters are searched and optimized by minimizing the cost function R_χ by our recently developed machine learning (ML) approach. This approach is based on combining particle swarm optimization (PSO), Gaussian process regression (GPR) and Bayesian optimization (BO). Particle swarm optimization (PSO) is a population-based stochastic

optimization algorithm proposed in 1995, motivated by intelligent collective social behavior of animals such as fish schooling or bird flocking behaviors [14-16]. Unlike gradient descent mechanism, no gradient information is required for PSO, making it easy to use in many optimization scenarios. The basic idea of PSO applied in our case can be described as follows: in PSO, a population of candidate parameter sets, called particles, moves through a multidimensional search space in search of the optimal solution. Each particle maintains its position and velocity, which are adjusted iteratively based on its own best-known position (personal best) and the global best-known position within the swarm. Through this process of continuous adjustment and interaction, particles dynamically explore and exploit the solution space, gradually converging towards promising regions. It iterates until a stopping criterion is met, which is our defined cost function. However, PSO is efficient to identify local regions around the global minimum. Thus, a more accurate approach is needed to finalize the parameter set. BO adeptly balances exploration and exploitation throughout its iterative process, skillfully navigating the solution space [17, 18]. It dynamically adapts its search strategy by incorporating insights from past observations, continually refining its approach to converge towards the optimal solution.

The optimization processes are illustrated in Figure 4-1. The initial parameters are mainly based on the classical SW potential. We defined p and q values for 2-body Se-Se parameters to have a target Se-Se bond length. Based on the defined cost function, compared ab initio reference and empirical forcefield, the parameters are first estimated by PSO. As shown in Figure 4-2(b), taking the parameter pair of $\beta_{\text{Ge-Se-Ge}}$ and $\lambda_{\text{Ge-Se-Ge}}$ as an example, PSO can provide an estimate value around 30eV and 10 eV respectively. As mentioned earlier, to reach a more accurate value,

GPR and BO are required to optimize in the region of local minimum, as shown in Figure 4-2 (c) and (d). As a result, the optimal forcefield parameters can be achieved, as shown in Table 4-1.

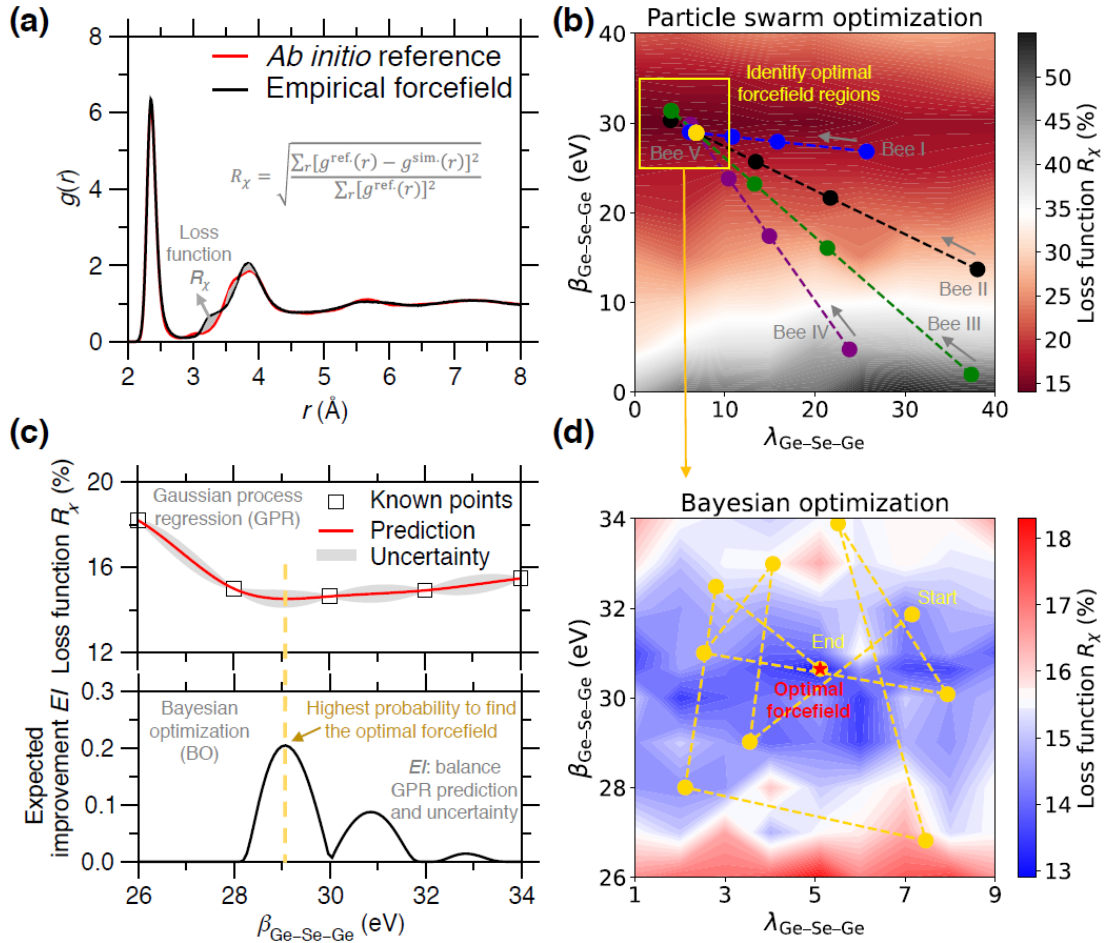


Figure 4-1: (a) Total pair distribution function (PDF) $g(r)$ from Ge_xSe_{1-x} Ab initio reference and our empirical Ge_xSe_{1-x} forcefield offering minimum R_χ . (b) Schematic showing how the algorithm of particle swarm optimization (PSO) provides a rough estimate of the parameter sets. Particle positions are adjusted at each iteration from a set of stochastic velocities calculated at the current iteration. (c) Gaussian process regression (GPR) and Bayesian optimization (BO) balance together to determine the parameters. (d) BO is applied to finalize the parameter set as it is more reliable when exploring local regions to identify global minimum.

Table 4-1: Optimized forcefield parameters

Two-body parameters								
i-j	ϵ_{ij} (eV)	σ_{ij} (Å)	a_{ij}	γ_{ij}	A_{ij}	B_{ij}	p_{ij}	q_{ij}
Ge-Ge	1.6300	2.1810	1.80	1.200	7.049556277	0.6022245584	4.0	0.0
Ge-Se	2.1304	1.9744	1.80	1.200	7.049556277	0.6022245584	4.0	0.0
Se-Se	2.1201	1.9954	1.80	1.289	18.75331000	1.0000000000	8.0	4.0
Three-body parameters								
i-j(center)-k	$\lambda_{ijk} \epsilon_{ijk} (= \lambda_{ijk} \epsilon_{ij})$ (eV)			θ_{ijk} (°)		β_{ijk} (eV)		
Ge-Ge-Ge	34.3881			109.47		0.0000		
Ge-Ge-Se	39.1907			109.47		0.0000		
Se-Ge-Se	66.9056			109.47		2.9666		
Ge-Se-Ge	10.8913			109.47		30.6475		
Ge-Se-Se	45.1218			109.47		40.7740		
Se-Se-Se	36.5922			109.47		55.6805		

We then adopt the optimized parameters to the SW potential to plot out the functions. Based on the experimental results, we can validate the rationality of these parameters. As shown in Figure 4-1(a), the Se-Se curvature is set to be abrupt compared to Ge-Ge and Ge-Se, mainly due to the experimental results showing that the Se-Se bond length is limited in a small range. For 3-body angular term, Ge-Se-Ge should be more flexible when the angle deviates from 109.47 degrees, which corresponds to a less energy increment, compared to Se-Ge-Se, as shown in Figure 4-1(b). Also, the radial penalty term β for Se-Ge-Se and Ge-Se-Ge shows a great difference, as illustrated in Figure 4-1(c).

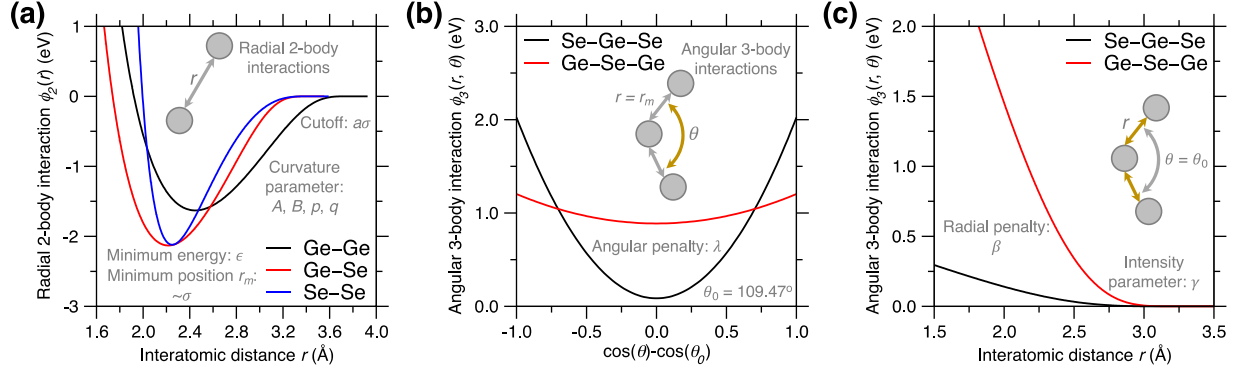


Figure 4-2: Forcefield visualization of (a) 2-body Ge-Ge, Ge-Se, Se-Se interaction potential. (b) 3-body interaction potential as the function of $\cos \theta_{ijk} - \cos \theta_{oijk}$. (c) 3-body potential as the function of interatomic distance r .

4.3 Results

To validate the accuracy of the empirical $\text{Ge}_x\text{Se}_{1-x}$ forcefield, pair distribution functions (PDFs) of the forcefield are compared to ab initio references. In Fig. 3 (a-d), four compositional ratios of Ge atom configurations are selected and compared with ab initio references on partial PDF $g_{\text{GeSe}}(r)$, $g_{\text{SeSe}}(r)$, $g_{\text{GeGe}}(r)$, and total PDF. Overall, the results match well except for $g_{\text{GeGe}}(r)$. In $\text{Ge}_x\text{Se}_{1-x}$ glass ab initio simulation, as shown in Figure 4-3(c), the configuration appears a great portion of edge sharing structures, which is not observed in experiment. The main reason is the relatively small number of atoms in the configuration, around 200 atoms, and the presence of edge sharing structures would become a prominent peak in partial PDF [5]. Thus, the mismatch in Figure 4-3(c) is due to the limitation of ab initio results, and it in turn favors the empirical forcefield to be more realistic. Similarly, as shown in Figure 4-4, the structural factor compared between ab initio and empirical also exhibits good agreement. Although the structural factor

contains the same information as the PDF, it emphasizes more on the medium-range order within the range of 0 to 4.

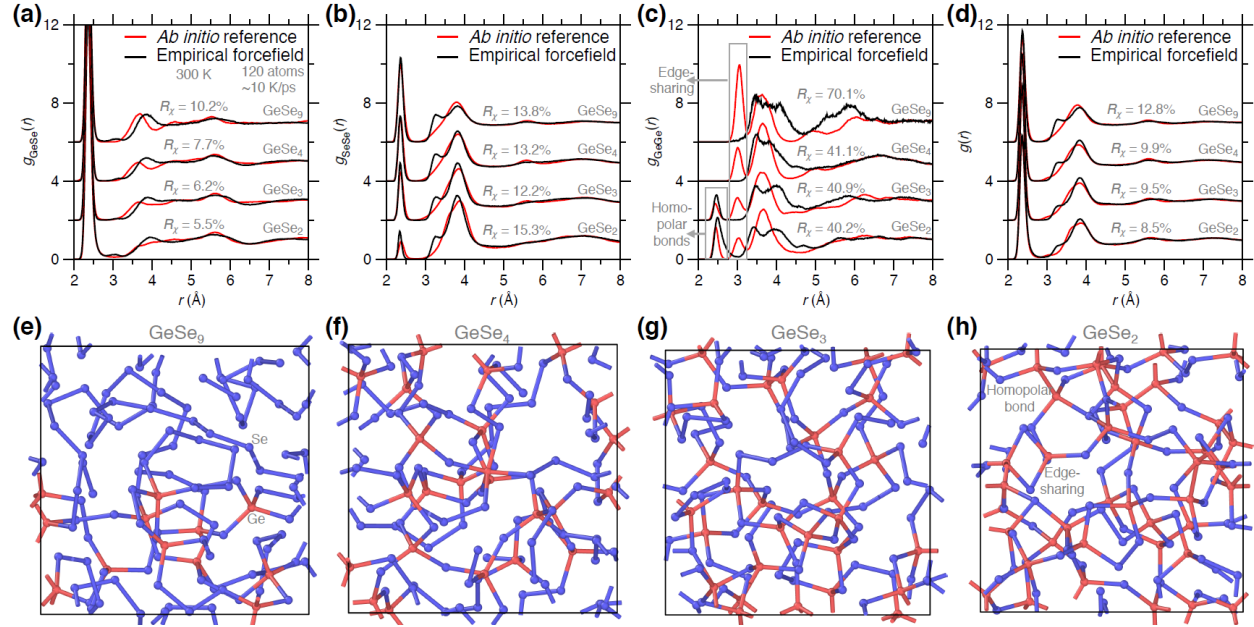


Figure 4-3: (a-d) Comparison of pair distribution function computed by *ab initio* and classical MD. (e-h) Atomic configurations generated by classical MD.

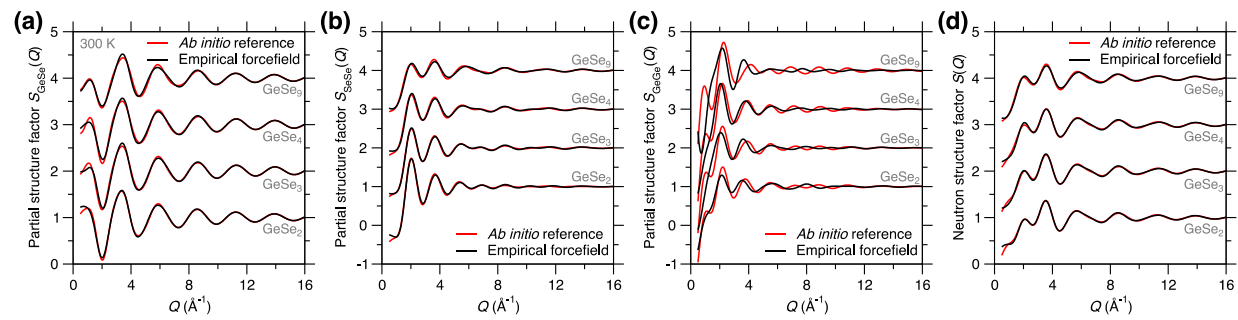


Figure 4-4: Comparison of neutron structure factor computed by *ab initio* and classical MD.

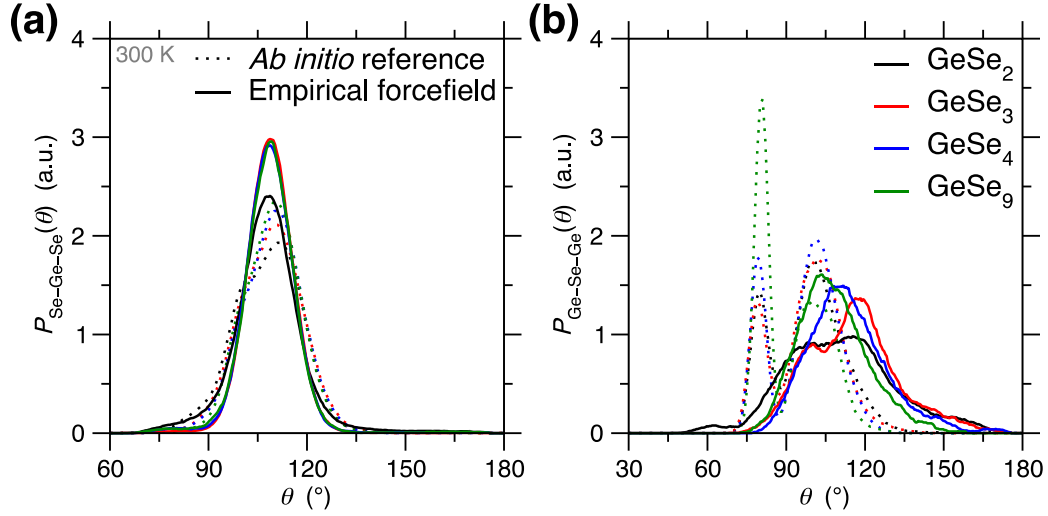


Figure 4-5: Comparison of bond angular distribution computed by ab initio and classical MD.

As shown in Figure 4-5, the bond angular distribution has been compared between the empirical forcefield and ab initio simulation. The Se-Ge-Se angles in empirical forcefield are in good agreement ab initio simulation as shown in Figure 4-5(a), while the Ge-Se-Se angles are shifted to higher angles for empirical forcefield as compared to ab initio simulation as present in Figure 4-5(b). As mentioned previously, the small Ge-Se-Ge angle around 80 degrees mainly comes from the edge sharing structure, which is over prominent in ab initio simulation.

Now the empirical $\text{Ge}_x\text{Se}_{1-x}$ forcefield has been validated to have a proper interatomic potential for $\text{Ge}_x\text{Se}_{1-x}$ glass, we adopt the previous proposed generic network model as a comparison. The most significant feature is the maximum value of enthalpic difference during thermal cycles, ΔH_{max} as the function of number of constraints. Figure 4-5 shows the hysteresis curve under different cooling rates. It exhibits a similar trend as the generic ΔH_{max} curve where the minimum reached at $\langle nc \rangle$ is around 3. However, the transition from flexible to isostatic appears to be less abrupt and the isostatic to stressed-rigid transition appears to be more sudden. The

reason for the relatively smooth transition at low $\langle nc \rangle$ mainly due to the great volume difference in the generic model, while the realistic model uses almost the same volume for all compositional ratios. The sudden increase at high $\langle nc \rangle$ reveals the effect of chemistry, that emphasis the interatomic effect of extra Ge atoms.

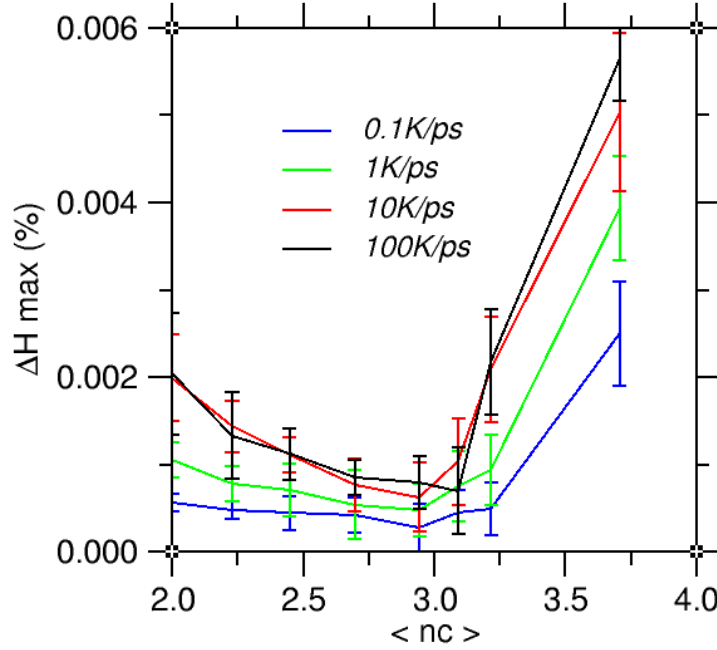


Figure 4-6: Maximum of ΔH as the function of number of constraints under different cooling rates.

In glass physics, fragility characterizes how rapidly the dynamics of the supercooled liquid slow down as it is cooled toward the glass transition. The fragility m reflects the slope of the viscosity or relaxation time of a glass with temperature as it approaches glass transition temperature [19, 20]. The fragility is defined as follow:

$$m = \left(\frac{\partial \log_{10} \eta}{\partial \left(\frac{T_g}{T} \right)} \right)_{T=T_g}$$

where η is the viscosity, T_g is the transition temperature. If we put fragility m into the enthalpic Gaussian curve function, which expressed as:

$$\Delta H = H_{max} \exp \left[\frac{-(T - T_{max})^2}{2\Delta T^2} \right]$$

Where H_{max} is the maximum extent of enthalpy change, T_{max} is the temperature corresponding with H_{max} , ΔT is the temperature range of the relaxation. We can get the relationship that ΔT is proportional to T_{max}/m , which indicates the narrower glass transition temperature corresponds with a higher fragility and vice versa. As shown in Figure 4-7, the effect of fragility appears as a fragility window as the function of Ge ratio of composition. This result matches well with experimental data while the simple generic model cannot retrieve such behavior. The key is the empirical model accurately captures the transition temperature T_g for each configuration compared with the simple model, which cannot provide relatively reasonable glass transition temperatures. To validate the fragility window, additional evidence can be acquired. Based on the Gibbs–DiMarzio theory of the glass transition [21] and the further developed temperature dependent topological constraint model [22], glass fragility can be directly computed solely on the scaling of the topological degrees of freedom with temperature. In another word, fragility is directly correlated with the speed of constraint breaking as temperature increases. During the simulation, the number of constraints can be monitored at each temperature, and it can be plotted as shown in Figure 4-8. From this plot, we only care about the slope of the curve at transition temperature where $T_g/T = 1$ since it represents the speed of constraints breaking. Thus, the effect of fragility as the function of Ge ratio of composition can be gained as shown in Figure 4-9. It

appears a similar deep around 20% Ge concentration and supports the fitted results of effect of fragility window.

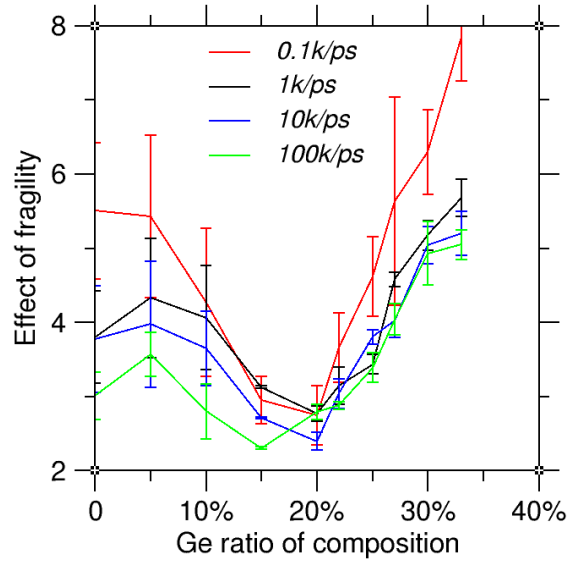


Figure 4-7: Effect of fragility as the function of Ge ratio of composition, under different cooling rates.

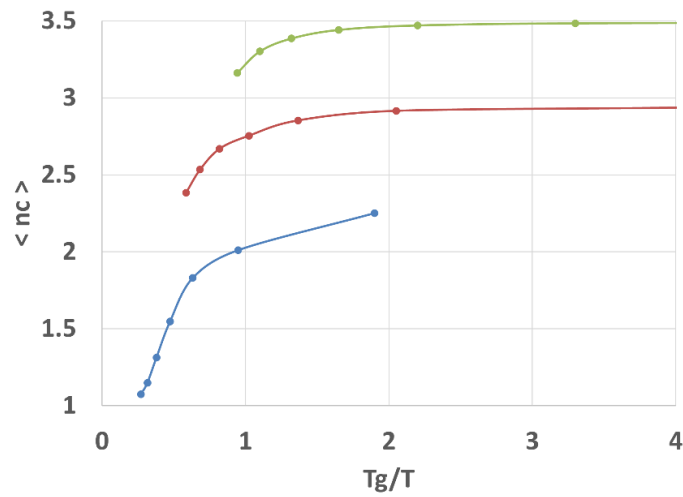


Figure 4-8: The $\langle nc \rangle$ as the function of T_g/T for three glasses with Ge atom ratio of composition for 5% (blue), 20% (red) and 33%(green) respectively.

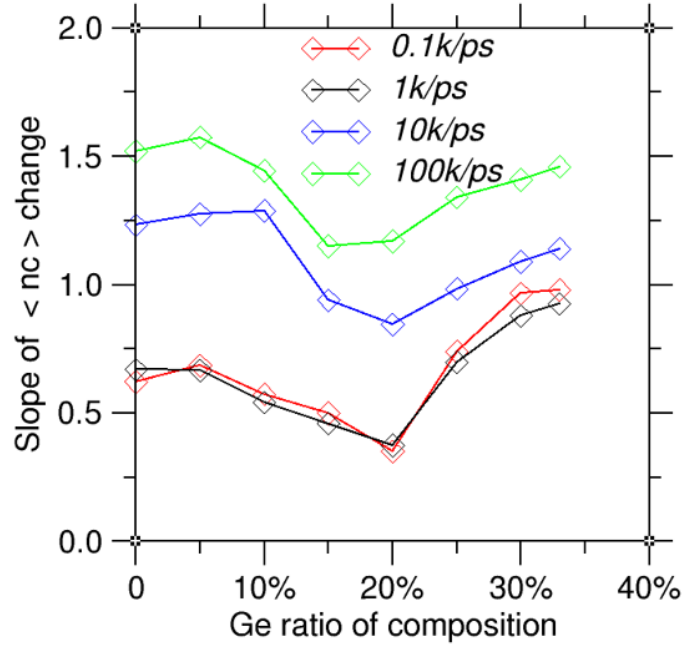


Figure 4-9: The $\langle nc \rangle$ slope of change as the function of Ge ratio of composition where $T_g/T = 1$, under different cooling rates.

To understand what causes the discrepancy between these two models, we start reviewing their parameters of SW potential. For the simplified model, since the two types of atoms share the same 2-body parameters, it provides less energy penalty for B atom, which is Se atom in empirical model, as expected. As shown in Figure 4-2(a), Se-Se bond length should be trapped in a smaller range compare with Ge-Se and Ge-Ge, with abrupt energy increment after length deviation. Thus, the simple model would have larger B-B atom bond length than expected and yield a larger volume difference as the function of compositional ratio. For 3-body parameters, the simple model utilizes 109.5 degree of X-A-X and 160 degrees for X-B-X while the empirical model uses 109.5 degree for both types of atoms. As shown in the previous studies both experimentally and theoretically [5, 19, 20], the angle supposes to be around 109.5 for both

atoms. The reason for the simple model utilizing 160 degree is the absence of extra repulsive forces to keep the target coordination and avoid clustering [21-24]. Consequently, the large angle expands the configuration volume and harms the glass T_g trend as the function of connectivity. However, the large volume in simple model favors the abrupt change of enthalpic curve where the empirical model lacks, where the flexible to isostatic transition happens. This indicates the parameters in empirical forcefield cannot capture the high flexibility of lower Ge atom concentration glasses.

4.4 Conclusions

Overall, we parameterize an empirical $\text{Ge}_x\text{Se}_{1-x}$ potential with machine learning methods and validate it with ab initio reference. This forcefield shows a better structural agreement with experimental results compared to ab initio reference by breaking the simulation box size limitation. As the potential is in the form of SW potential, same as our previously constructed generic simple model, a comparison is made between the empirical and simple models to reveal the effect of the extra parameterization, which indicates effect of chemistry. The difference of the hysteresis enthalpic curve highlights the effect of the box size on the atomic mobility in simple model and the higher rigidity of with the increment of Ge atom in empirical model. The discussion regarding the parameters shows the main reason comes from the 2-body bond length term for the 2-folded atom and large 160 degree applied in 3-body term for the simple model. Moreover, the empirical forcefield successfully presents the fragility window observed in $\text{Ge}_x\text{Se}_{1-x}$ glass while the generic model cannot. The fragility window has been proved in the way of monitoring the slope of change in constraints breaking. The empirical $\text{Ge}_x\text{Se}_{1-x}$ glass model

shows superior ability in revealing glass fragility. The comparison between the empirical model and the generic network model uncovers new insights into their atomic structure.

4.5 Reference

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Chapter 5. Summary and Outlook

Owing to the high efficiency and accuracy, MD simulation in glass structure has drawn extensive attention in the past few decades. Overall, in this thesis, two models are studied, a generic simple model and a realistic empirical $\text{Ge}_x\text{Se}_{1-x}$ model. In the aspect of physics features, we start with structural and thermodynamic features, and later extend to energy landscapes signatures and finally link to rheological properties.

In chapter 2, I developed a simple network glass model based on SW potential. In the spirit of Kob-Andersen Lennard-Jones (KALJ) potential, which serves as a standard glass model for year, the simple model is designed with enough simplicity while maintaining the basic tetrahedral building block for 2-folded and 4-folded mixture. After tuning the parameters to ensure homogeneity and reaching the proper coordination, the model has been validated to be a proper description of a generic glass model.

In chapter 3, based on the previous model, I studied the energy landscape signatures as the function of connectivity, which is nc . The configurations are shown to reproduce the hysteresis, identifying the regions of different rigidity, namely flexible, isostatic and stressed-rigid. Then the main contributions of these transitions are identified individually by MSD and stress/atom. The height of energy barrier effect on the rigidity has been discovered for the first time. Furthermore, relaxations under different rigidities are discussed and extended to medium range. To consolidate our conclusions, a dicing strategy is proposed to increase the sample size and reduce the effect of volume sizes.

In chapter 4, an empirical $\text{Ge}_x\text{Se}_{1-x}$ glass also based on SW potential is parameterized with machine learning. With the comparison with ab initio reference, the forcefield is examined to be a more proper description for $\text{Ge}_x\text{Se}_{1-x}$ glass, due to the limitation size of ab initio simulation. The simple model is used to compare with the realistic model, highlighting the effect of chemistry and the ability to reveal the effect of fragility. The fragility window shows great agreement with experimental data due to the accuracy of glass transition temperatures.

Further investigation can be applied based on our simple and empirical models. For the localized nc cubes, the percolation of rigidity can be further studied. Also, glass heterogeneity can be further discussed and explored. Based on the realistic model, as mentioned earlier, fine structures such as homopolar bond and edge sharing structures, can be investigated to see their effect.