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Stress Intensity Thresholds for Development of Reliable Brittle Materials

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ABSTRACT

Brittle material failure in high consequence systems can appear random and unpredictable at subcritical stresses. Gaps in our understanding of how structural flaws and environmental factors (humidity, temperature) impact fracture propagation need to be addressed to circumvent this issue. A combined experimental and computational approach composed of molecular dynamics (MD) simulations, numerical modeling, and atomic force microscopy (AFM) has been undertaken to identify mechanisms of slow crack growth in silicate glasses. AFM characterization of crack growth as slow as 10^{-13} m/s was observed, with some stepwise crack growth. MD simulations have identified the critical role of inelastic relaxation in crack propagation, including evolution of the structure during relaxation. A numerical model for the existence of a stress intensity threshold, a stress intensity below which a fracture will not propagate, was developed. This transferrable model for predicting slow crack growth is being incorporated into mission-based programs.

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ACRONYMS AND TERMS

Acronym/Term	Definition
MD	Molecular Dynamics
TCT	Topological Constraint Theory
AFM	Atomic Force Microscopy
Si ²	Silicon atom bonded to two other atoms
Si ³	Silicon atom bonded to three other atoms
Q _n	Silicon bonded to n bridging oxygen
NBO	Non-bridging oxygen
BO	Bridging oxygen
TBO	Three-bonded oxygen
G _{DISS}	Dissipation energy
SEM	Scanning electron microscopy
E	Young's (elastic) modulus
G	Shear modulus
K	Bulk modulus
ν	Poisson's ratio
γ	Surface energy
T _{melt}	Melting temperature
t _{melt}	Melting time
T _{anneal}	Annealing temperature
t _{anneal}	Annealing time
CTE	Coefficient of thermal expansion
T _g	Glass transition temperature
LEFM	Linear elastic fracture mechanics
NVT	Microcanonical ensemble
NPT	Isothermal-isobaric ensemble
TTS	Time-temperature-superposition
ps	Picosecond
fs	Femtosecond
FJC	freely joined chain
k _B	Boltzmann Constant

Acronym/Term	Definition
E_{total}	Total energy
E_{bond}	Bond energy
E_{over}	Over-coordination energy penalty
E_{under}	Energy penalty for unbound π electrons
E_{LP}	Energy for lone pairs
E_{val}	Valence angle energy term
E_{pen}	Energy penalty from stable systems with double bonds
E_{tors}	Torsion angle energy term
E_{conj}	Conjugate component of the molecular energy
E_{vdW}	Long-range van der Waals interaction
E_{coul}	Shielded Coulombic interaction
DCB	Double cantilever beam
RH	Relative humidity
DCDC	Drilled compression double cantilever
TPB	Two-point bend
DI	De-ionized water
DSC	Differential scanning calorimetry
TMA	Thermal mechanical analysis
DMA	Dynamic mechanical analysis
SEPB	Single-edged pre-crack beam
ToF-SIMS	Time-of-flight secondary ion mass spectroscopy
RUS	Resonant ultrasound spectroscopy
FIB	Focused ion beam
n_{TPB}	Dynamic fatigue parameter

1. INTRODUCTION

Brittle material failure in high consequence systems can appear random and unpredictable at subcritical stresses. Gaps in our understanding of how structural flaws and environmental factors (humidity, temperature) impact fracture propagation need to be addressed to circumvent this issue. We propose to drastically limit uncertainties in predicting glass fracture by developing a fundamental physics-based model to bound lifetime predictions of brittle components and metrics for the future design of reliable glass parts based on processing and service conditions.

In contrast to dynamic crack growth, which occurs above the critical stress intensity factor and is primarily controlled by stress, the fundamental mechanisms controlling slow crack growth are a matter of debate. Current theories include environmentally assisted cracking, crack-tip blunting, local plasticity, and environmental conditions.¹⁻⁵ Of these, the most common and well-accepted is increased slow crack growth in the presence of a reactive environment. Also termed chemo-mechanical fracture, stress corrosion cracking, or environmentally assisted fracture,⁶⁻⁹ this process typically occurs in the presence of humidity, with water diffusing through the crack and sequentially breaking highly strained bonds at the crack tip causing slow crack growth, as shown in Figure 1-1.¹⁰

Amorphous systems are unique in that their far-from equilibrium structure is a continuous driver for structural relaxation that can inform slow crack growth without the presence of a reactive environment. Internal residual stress can be large, with values in excess of 60 MPa reported in perovskite films.¹¹ In amorphous oxides stress relaxation is temperature dependent and follows a stretch exponential decay function. Welch et al. evaluated relationship for strain during aging of an ion-exchanged glass at room temperature, with a measured linear strain of 1×10^{-5} over 1.5 years of aging.¹² The long tail of the relationship indicates that structural relaxation occurs, even at low temperatures, for the lifetime of the material. Trap models provide physical insight into the stress relaxation process, where a complex potential energy landscape results in local and disconnected minima that trap metastable structures.¹³ Lifetimes and stabilities of these trap sites vary across the amorphous oxide structure, slowing the relaxation process as the least stable structures are removed and the properties of the system are dominated by the lowest energy thermodynamic state.

Dynamically evolving stress gradients, influenced by the presence of a reactive environment, can also influence slow-crack growth rates. Fracture surfaces are intrinsically high energy, and reactive environments are well known to relax fracture surfaces due to hydroxylation.¹⁴ Experimental secondary ion mass spectroscopy measurements identified that hydroxylation of silica fracture surfaces occurs within the first few ps of exposure,¹⁵ while classical MD simulations identified that the alteration of the surface structure causes relaxation up to 10 Å into the surface.¹⁶⁻¹⁷ Slow crack growth in amorphous oxides is controlled by reactions that occur within the nanometer scale inelastic

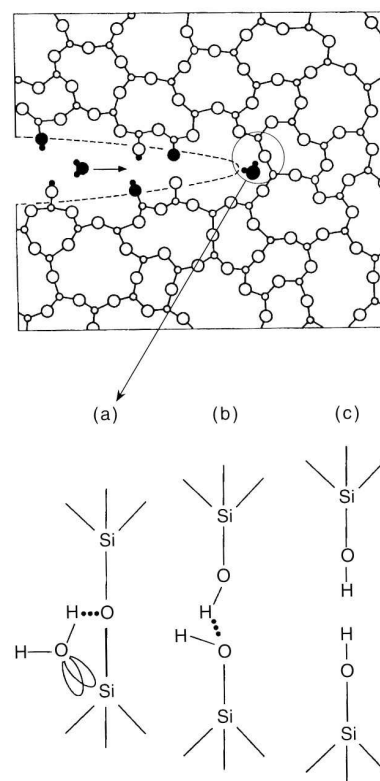


Figure 1-1: Theory of slow crack growth via reaction between water molecules and the -Si-O-Si- bonds at the crack

region at the crack tip,¹⁸⁻²⁰ so that an alteration of the first 10 Å of the surface alters the stresses in 20-30% of the region that controls slow crack growth.

In amorphous oxides, slow crack growth is controlled by the local microstructure, despite the lack of grain structures, with differences in the local coordination changing the fracture properties. Amorphous oxides can be separated into *strong* and *fragile* systems, based on the divergence of the Arrhenius relationship between viscosity and temperature. Fragility can be evaluated on a per-atom basis, using the concepts of mechanical constraints. TCT has been recently introduced to analyze properties of amorphous oxides. In TCT, the number of constraints causes a structural unit to be classified as (i) flexible, (ii) isostatic, or (iii) stress rigid. Fewer constraints results in a weak flexible structure, while an over constrained or stress-rigid system introduces stronger but more brittle constituents. TCT is commonly used for prediction of material properties based on the *average number* of constraints in the system.

In a few cases, TCT can also be integrated with local compositional heterogeneity in amorphous oxides that manifests on the nanometer scale, distinct from larger scale phase separation.²¹ Local compositional heterogeneity does not impact the macroscopic structure but influences short-range properties.²² In amorphous oxides, local compositional heterogeneity has been reported in Ca²⁺ containing glasses,²³ resulting in the formation of Si-rich and Ca-rich regions in highly modified amorphous oxides used for nuclear waste disposal²⁴ and Al-O-Al nanoclusters in modeling of a silica-alumina fibers.²⁵ For evaluation of fracture properties, Wang et al. evaluated nano ductility via TCT²⁶ and identified that under tension a simulated sodium-silicate amorphous oxide preferentially fractured through regions with higher sodium content and lower constraints, as shown in Figure 1-2.²⁶

When a crack encounters a region of high strength, TCT and related compositional based theories are unable to explain why a crack would continue to propagate. TRT uses a series of increasing metastable states that allow for slow crack growth propagation events following thermal activation. The states are quasi-stationary so that the jump frequency is proportional to the probability of a propagation event. Such methods require an understanding of the activation energy for these events that allow for escape from each metastable equilibrium - information that is complicated in amorphous oxides with thousands of individual short and intermediate range structures. Additionally, TRT provides no physical or chemical insight into what causes the changes in activation energy other than temperature.

LEFM, stochastic strength analysis, and viscoelastic modeling have all been applied to brittle fracture and have provided benchmarks for material lifetimes. Existing methods to avoid fracture failure have included limiting surface flaws, isolating the material from reactive environments, and decreasing inherent external stresses. In contrast to other brittle materials, glass is non-crystalline and contains structural flaws that are distinct from and behave differently than the more familiar dislocations, grain boundaries, and other flaws commonly found in crystalline materials. Additional

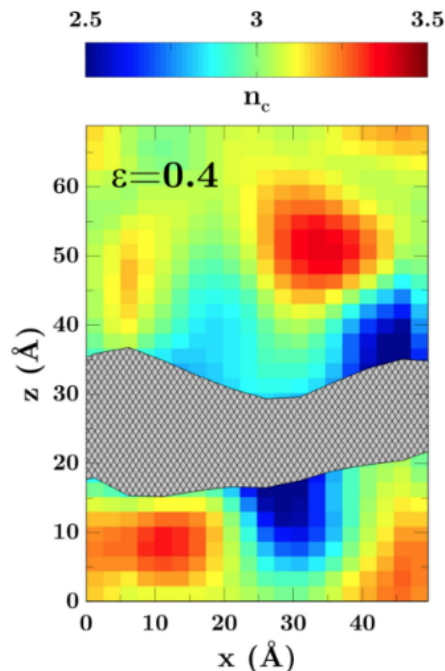


Figure 1-2: Contour maps of the local number of constraints per atom (n_c) in a 20% Na₂O sodium-silicate compounds with 0.4 strain.²⁶

mechanistic insight into rare events, such as ion migration, surface-environment interactions, or bond-switching events, are required to accurately describe the fracture process.

Over the last twenty years, characterization and computational capabilities have advanced, allowing scientists to investigate mechanisms that govern fracture initiation and propagation that were previously below detection limits. To identify (1) the lower bound of crack velocities and (2) mechanisms that cause delayed glass fracture, we will apply recent advances in both experimental and computational methodologies. Previous limitations in measuring subcritical fracture velocities will be overcome using AFM for identification of nanoscale propagation events in slow moving cracks²⁷⁻²⁸. By taking advantage of SNL-developed diffusion bonded bi-beam samples,²⁹ controlled, stable crack growth under known stress conditions can be explored. This data will be used to calibrate parameters for a crack velocity model based on transition rate theory, which describes the frequency at which stochastic excitations push a system from one metastable state to another. The crack velocity model parameters relate to individual bond breaking events, which occur on a time and length scale directly accessible by MD modeling. The crack velocity model then acts as a bridge from atomistic (ps/Å) to experimental (years/mm) time frames. Atomistic models will build on established expertise in modeling glass fracture³⁰⁻³² to separate crack propagation.

The outcome of the project will be a validated physics-based model of subcritical crack growth, based on the mechanisms that control brittle fracture at subcritical stress intensities. This effort will still result in a mechanistic understanding and improved crack velocity data of subcritical fracture in brittle materials reducing uncertainty and improving the ability to predict failure at long lifetimes.

2. ACCOMPLISHMENTS

2.1. Journal Articles

2.1.1. Published

Cover: Rimsza, Jessica M., Scott J. Grutzik, and Reese E. Jones. "Inelastic relaxation in silica via reactive molecular dynamics." *Journal of the American Ceramic Society* 105.4 (2022): 2517-2526.

Special Issue: Rimsza, Jessica M., and Reese E. Jones. "Fracture mechanisms of sodium silicate glasses." *International Journal of Applied Glass Science: Glasses for tomorrow: Composition–structure–property relationships to accelerate the design of functional glasses* (2022).

Buche, Michael R., Meredith N. Silberstein, and Scott J. Grutzik. "Freely jointed chain models with extensible links." *Physical Review E* 106.2 (2022): 024502.

2.1.2. Submitted

Special Issue: Grutzik, Scott., Kevin T. Strong, and Jessica M. Rimsza. "Kinetic model of prediction of subcritical crack growth threshold in silicate glass" *Journal of Non-Crystalline Solids: International Year of Glass Celebration Issue* (2022)

Stevenson, Caralyn A., Sydney Scheirey, Jordan Monroe, Richael Zhang, Ethan Main, Olivia Jones, WeiBin Cheah, Sarah Park, Briana Nobbe, Isha Sura, Jessica M. Rimsza, and Stephen P. Beaudoin. "Incorporating the effect of surface and particle properties towards adhesion in humid environments through the enhanced centrifuge method" *Colloids and Surfaces A* (2022)

2.1.3. In Progress

Nakakura, Craig Y., Kelly S. Stephens, Jessica M. Duree, Jamar T. Rogers, Kevin T. Strong, Scott G. Grutzik, Jessica M. Rimsza. "Micron scale fracture propagation in sodium silica glass" *Journal of the American Ceramics Society* (2022)

Buche, Michael and Scott J. Grutzik. "A statistical mechanical Model for crack growth" *Physical Review E* (2022)

Weyrauch, Noah M., Kevin T. Strong, and Richard K. Brow. "Sub-critical crack growth and fatigue of alkali silicate glasses" *Journal of the American Ceramics Society* (2022)

2.2. Copyrights

2.2.1. Software

Buche, Michael R. and Scott J. Grutzik. "uFJC: the Python package for the uFJC single-chain model." [Zenodo](#) (2022).

Buche, Michael R. and Scott J. Grutzik. "statMechCrack: the Python package for a statistical mechanical model for crack growth." [Zenodo](#) (2022).

2.3. Post-Docs and Students

2.3.1. Post-Docs

Michael Buche (1542) – Michael has a PhD in Theoretical and Applied Mechanics from Cornell University. His primary focus is on the development of numerical models for modeling of brittle fracture using statistical mechanics. He was hired for this project and converted to staff in FY22.

2.3.2. Interns and Graduate Student

Noah Weyrauch (Missouri University of Science and Technology) – Noah is a MS student in Ceramic Engineering at Missouri University of Science and Technology working with Dr. Richard Brow. His project is on the evaluation of environmental and chemical effects on slow crack growth in silicate glasses.

Jamar Rogers (Mississippi State University) – Jamar is an undergraduate in mechanical engineering at Mississippi State University. He supported this project through evaluation of slow crack growth in silicates measured via AFM.

Caralyn Stevenson (Purdue University) – Cara was a PhD student in Chemical Engineering at Purdue University working with Dr. Stephen Beaudoin. Her project focused on the capillary effects between silica particles and silica surfaces as a function of humidity.

2.4. Conference Presentations

2.4.1. 2020

Invited - Rimsza, Jessica M., and Jincheng Du. “Atomistic computer simulations of the dissolution of inorganic glasses”. *2020 Virtual Glass Summit* August 2020

2.4.2. 2021

Rimsza, Jessica M. Craig Nakakura, Scott Grutzik, and Kevin T. Strong. “Atomistic fracture mechanisms in sodium silicates.” *American Ceramics Society Glass and Optical Materials Division Meeting / 4th Pacific Rim Conference on Ceramic and Glass Technology*, December 2021

Strong, Kevin, T., Craig Nakakura, Jessica Depoy, Kelly Stephens, Thomas Diebold, Scott Grutzik, and Jessica Rimsza “Investigation of Slow Crack Growth of Sodium Silicates with AFM” *American Ceramics Society Glass and Optical Materials Division Meeting / 4th Pacific Rim Conference on Ceramic and Glass Technology*, December 2021

Grutzik, Scott J. “Kinetic Model for Environmentally Assisted Crack Growth Threshold” *American Ceramics Society Glass and Optical Materials Division Meeting / 4th Pacific Rim Conference on Ceramic and Glass Technology*, December 2021

2.4.3. 2022

Invited - Rimsza, Jessica M., Kevin T. Strong, Craig Nakakura, Jessica Duree, Kelly Stephens, and Scott Grutzik. “Slow crack growth in sodium-modified silicate glasses” *American Ceramics Society Glass and Optical Materials Division Meeting*, May 2022, Baltimore, MD

Weyrauch, Noah M., Kevin T. Strong, and Richard K. Brow. “A Comparison of Subcritical Crack Growth Behavior and the Dynamic Fatigue Parameter for Alkali Silicate Glasses” *American Ceramics Society Glass and Optical Materials Division Meeting*, May 2022, Baltimore, MD

2.5. Other Presentations/Deliverables

Book Chapter - Rimsza, Jessica M., et al. "Simulations of Glass–Water Interactions." *Atomistic Simulations of Glasses: Fundamentals and Applications* (2022): 490-521.

Planned conference presentation: Buche, Michael R., et al. “Low-temperature statistical thermodynamics by an asymptotic method.” *APS March Meeting* (2023).

3. INELASTIC RELAXATION IN SILICA GLASS

3.1. Overview

Silica glass exhibits rate-dependent and irreversible processes during deformation and failure, resulting in inelastic effects. MD simulations of structural relaxation surrounding a crack tip in silica glass were performed at four different temperatures (100-900 K) using a reactive force field. Per-atom stresses were found to relax during the simulation, with the highest stress relaxation occurring at 900 K. Stress relaxation was radially dependent relative to the crack tip, with stress dissipation occurring primarily within a 25-30 Å inelastic region. Within 10 Å of the crack tip, the defect concentration decreased from 0.18 #/nm² to 0.09 #/nm² during inelastic relaxation at 900 K. Conversely, the defect concentration 20 Å from the crack tip increased from 0.105 #/nm² to 0.118 #/nm² at 300 K, and from 0.113 #/nm² to 0.126 #/nm² at 600 K, which formed a defect-enriched region ahead of the crack tip. The difference in defect concentrations suggests the existence of a stress mediated defect migration mechanism, where defects move away from the crack tip during inelastic relaxation. Additionally, defect speciation indicated that undercoordinated silica defects, such as NBO, were removed through the formation of higher coordination defects during relaxation. Overall, stress relaxation causes changes in the defect concentration profile near the crack tip, with the potential to alter silica glass properties in the inelastic region during relaxation. This chapter is adapted from the following publication: Rimsza, Jessica M., Scott J. Grutzik, and Reese E. Jones. "Inelastic relaxation in silica via reactive molecular dynamics." *Journal of the American Ceramic Society* 105.4 (2022): 2517-2526. (<https://doi.org/10.1111/jace.18177>)

3.2. Introduction

Vitreous silica commonly fails due to brittle fracture, leading to reliability concerns across a wide application range, including optics,³³ microelectronics,³⁴ and structural materials.³⁵ LEFM is commonly applied to predict failure of materials based on analytic solutions for the stress singularity at a crack tip³⁶ and evaluate fracture toughness in terms of the applied load and geometry. The material mechanisms that govern failure at an atomistic or microstructural level are contained in a process zone around the crack tip. When the size of this process zone is small compared to other relevant length scales, failure is interpreted in terms of a critical stress intensity factor, i.e., fracture toughness. In this case, crack growth is controlled by structural changes in an extremely local region of the crack tip due to inelastic effects. Inelasticity includes relaxation via unrecoverable relaxation events, such as coordination changes,³⁷ rather than elastic deformation via bond stretching, which is recoverable upon removal of the loading. Near-tip inelastic relaxation is a common feature of amorphous materials,³⁸⁻³⁹ and can influence their fracture properties.

In inorganic glasses, the process zone is generally restricted to a nanometer sized region surrounding a crack tip.⁴⁰⁻⁴¹ The small size of the process zone makes it challenging to observe with typical spectroscopic or microscopy methods, but some success has been identified through the application of AFM⁴² and via photon emission during silica glass fracture.⁴³ These methods observed what may be voids ahead of a crack tip, which coalesce to form a running crack.⁴⁴ Challenges remain in characterizing the inelastic zone and its impact on slow crack growth.

The small size of the process zone (a few nanometers) makes the inelasticity around the crack tip is well suited to investigation via MD simulations. Significant past work has been performed on mechanical and fracture properties of glasses using MD simulations.⁴⁵⁻⁴⁷ The most common simulation geometry omits existing cracks and uses applied uniaxial strain to identify changes in the short and medium range defect structure during loading⁴⁸⁻⁵⁰ and the formation of voids as a precursor

to failure.^{40, 51} MD simulations focusing specifically on crack growth have explored the introduction of a surface crack or voids prior to applied uniaxial strain.^{42, 49, 52-55} Similar methods using three different MD forcefields (Pedone, BKS, and Teter) have identified that crack branching is caused by cavity nucleation ahead of the crack tip.⁵⁶ A less common methodology has been the use of the LEFM solution as a far-field loading condition for a local atomistic region around the crack tip, minimizing finite size effects and allowing for dynamically evolving structural relaxation.⁴¹ Other efforts have focused on water as a medium for facilitating fracture growth in silica³⁰ due to the reported role of humidity on fracture,⁵⁷ but less effort has been on the evaluation of mechanisms of inelastic effects surrounding the silica crack tip. One previous work does consider the inelasticity of silica in bulk glasses,³⁷ but the unique stress conditions surrounding a crack tip were not evaluated. It is likely the case that the dominant mechanisms in the highly stressed and highly confined region around a crack tip are different than those that are dominant in bulk processes.

In this work, the mechanisms and temperature dependence of inelastic relaxation in silica glass were evaluated via reactive MD simulations. Elevated temperatures are used to connect to longer timescales in the inelastic relaxation process. The temperature dependence of the stress field, as well as the type and concentration of defects that are formed and removed, are reported, along with the potential impact on slow crack growth in silica.

3.3. Methods

The MD simulations in this study used the reactive force field ReaxFF⁵⁸⁻⁵⁹, which has been parametrized for silica.⁶⁰ ReaxFF allows for bond breakage and formation, which is necessary for MD simulations that include reactive species such as water⁶¹⁻⁶³ or when bond breakage is expected such as during fracture.^{31, 41} Because of its ability to model bond formation and breakage as well as approximate quantum mechanical effects, ReaxFF has a more complex functional form than force fields such as BKS⁶⁴, Tersoff⁶⁵, and ClayFF.⁶⁶ The functional form for total energy in ReaxFF is:

$$E_{\text{total}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{LP}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdW}} + E_{\text{coul}} \quad (3-1)$$

More details can be found in Reference 67. To investigate crack propagation in silica, thin, quasi-2D simulation cells (140 Å x 140 Å x 28 Å) were created through a melt-and-quench procedure. The initial configurations contained 38,400 atoms in a 2:1 oxygen to silicon ratio, which were heated to 4000 K and held for 100 ps to fully melt the structure. The systems were then cooled to 300 K at a rate of -5 K/ps. System densities were controlled during cooling at the experimental density of silica, 2.2 g/cm³,⁶⁸ through an NVT ensemble with a damping coefficient of 100 time steps and a time step of 0.5 fs. Following cooling, the density was allowed to fluctuate with an NPT ensemble alternated with energy minimization to achieve equilibrium systems. These equilibrated systems had a density of 2.187 g/cm³. All simulations were performed using the LAMMPS MD code with the USER-REAXC package using the Yeon and van Duin Si/O/H ReaxFF parameterization to be consistent with previous MD studies of silica fracture.^{30-31, 41}

For evaluation of inelastic relaxation, a perfect slit crack was created in the amorphous silica structure model by removing interactions between upper and lower sets of atoms separated by a plane extending halfway into the system (see Figure 3-1). To sample the isotropy expected in the amorphous systems, the original silica model was rotated by 90° three times, and a slit crack was introduced into the half plane of atoms to create four distinct systems. The average and standard deviation of the four simulations are then reported throughout the manuscript.

The crack was mechanically loaded by displacement of far-field atoms in a region outside a cylinder centered on the crack tip (see Figure 3-1). While the silica glass studied here is not expected

to behave identically to ductile metals, similar mechanisms of crack tip blunting do occur, and predicted process zones are expected to fall within the size of the active region simulated here. The atoms with prescribed displacement are fixed to maintain the loading over the course of the simulation. The displacement field was taken from the classical LEFM continuum solution for a semi-infinite slit crack in mode I (tension) loading, which is spatially varying and is parameterized by the stress intensity factor K_I .⁶⁹ The loaded slit crack develops a stress singularity that is characteristic of all classical cracks prior to relaxation,⁷⁰ compared with notch geometries.⁷¹⁻⁷² This methodology was demonstrated in evaluation of the J-integral during fracture for atomistic slit cracks.³² G is 25.06 GPa and the Poisson's ratio (0.31) were used for the far-field loading plain strain mode I tension based on previous reports using the same ReaxFF force field.³⁰

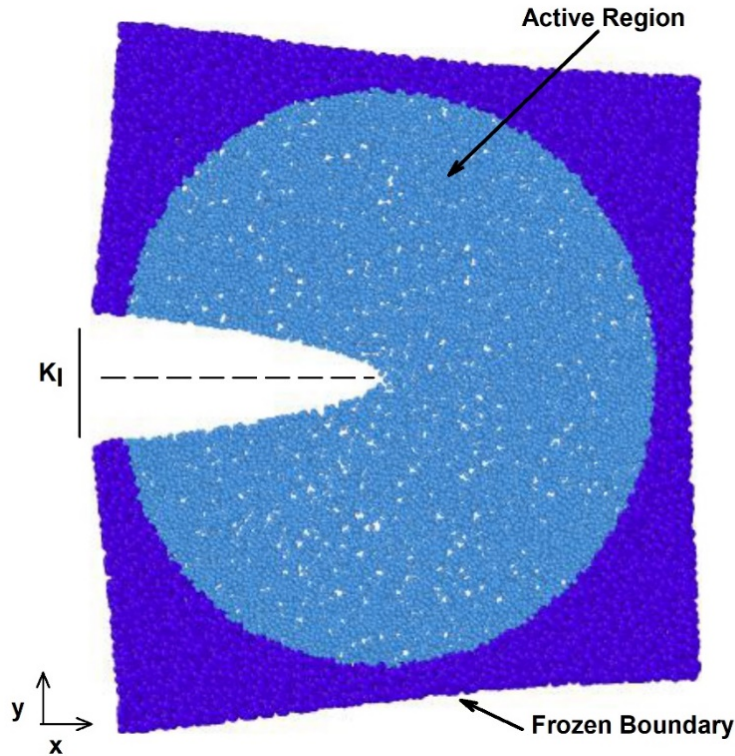


Figure 3-1: Snapshot of the silica structure with a loaded slit crack. The half plane where the bonds are broken is included as a dashed line. The active inner region where atoms are allowed to move (light blue), in contrast with the outer frozen boundary region (dark blue).

Via the prescribed displacement field, the crack was first opened in one step to a width of 6 Å at the widest point (K_I value of $2.24 \times 10^{-2} \text{ MPa}\sqrt{\text{m}}$). Following crack opening, relaxation of the interior active region was performed, while leaving the region with prescribed displacement fixed. Alternating minimizations and low-temperature NPT relaxations were performed to reach a relaxed structure. Following the formation of the slit crack, the structure dynamics were simulated, without further loading, at either 100 K, 300 K, 600 K, or 900 K for 500 ps. Higher temperatures were associated with accelerated relaxation due to the ability to overcome kinetic barriers⁷³ and has been previously used to investigate evolving silica-gel systems.⁶¹ The system temperature was controlled with a Nosé-Hoover thermostat, and no radial temperature variation was observed during the simulations.

Defect structures were identified through the evaluation of interatomic distances, using a 2.25 Å cut-off for Si-O distances, which has been previously used in MD simulations of silica using a ReaxFF force field as the first minimum in the Si-O pair distribution function.^{32, 74} An ideal oxygen atom would be bound to two silicon atoms, and a silicon atom would be bound to four bridging oxygen atoms. Alternative coordination structures, such as an oxygen atom bound to only one silicon or a silicon bound to three BO and one NBO are classified as defects and are discussed later in the chapter. The crack length was defined as the length of the horizontal line from the boundary of the system to the edge of the silica through the vacuum region. This method identifies overall changes in the length of the empty space that defines the crack, rather than using other recently reported methods based on the observed displacements and the stress intensity factor.⁷⁵

3.4. Results

Temperature is expected to significantly impact relaxation⁷⁶, since a higher temperature accelerates the dynamics and provides energy to overcome kinetic barriers.⁷³ Here, we average the per-atom stress normal to the crack face (S_{YY}) to identify changes in per-atom-stresses as a function of temperature and also of distance from the crack tip. In the case of temperature dependence, the per-atom S_{YY} stresses are averaged in a disk-like region within the first 50 Å of the crack tip. For radial dependence of S_{YY} , the per-atom stresses are averaged within 10 Å wide annular bins (e.g. for atoms between 20 Å and 30 Å from the crack tip). Overall, the least amount of relaxation occurs in the 100 K simulation, ~2%. As the temperature increases, the stress relaxation increases to ~22% at 300 K, ~40% at 600 K, and ~50% at 900 K following 500 ps of relaxation. The amount of stress dissipation also varies radially, which can also identify the size of the inelastic region. We find that the maximum decrease in stress occurs 20 Å away from the crack tip, with stress decreasing by ~70% over the course of the 500 ps simulation. See the exponential decay fits of the stress as a function of radial distance for the 600 K simulation in Figure 3-2, inset. Note that we average over the angular dependence of the stress in the quasi-2D samples. In comparison, 30 Å away from the crack tip the stress decreases by 30%. Even farther from the crack tip (40 Å and 50 Å) the curves begin to overlap, indicating a convergence in the stress relaxation. One note is that within 10 Å of the fracture tip, a small increase in stress occurs. We postulate that due to localized blunting of the crack tip, stress becomes more aligned with the crack face normal direction; thus, the apparent increase in stress at the 10 Å radius. Generally, the first 10 Å of the crack tip are the most chemically active, which can complicate analyses. Further from the crack tip, where less defect formation and/or bond breaking is occurring, a more consistent trend is observed.

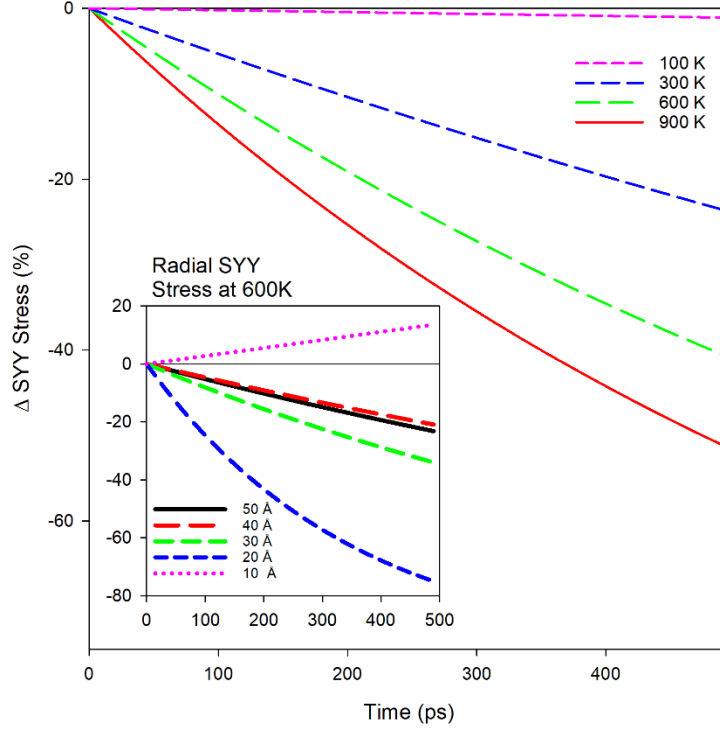


Figure 3-2: Exponential decay fit of the percent change in per atom stress normal to the crack face (S_{YY}) in the inelastic region (up to 50 Å radius) at varying temperatures (100 K, 300 K, 600 K, 900 K). Inset: Radial dependence of S_{YY} per-atom stress relaxation at 600 K.

Next, we consider the shape and magnitude of the stress field. Figure 3-3 includes the binned per-atom-stress around the crack tip, which shows that the stress is concentrated ahead of the crack tip. The stress distributions are consistent with the linear elastic solution for this far field loading conditions, particularly for the 100 K simulation. Similar stress patterns were reported with this ReaxFF force field for dynamically loaded silica in vacuum.⁴¹ As the temperature is increased the stress decreases, with the stress concentration migrating further ahead of the crack tip (see 600 K panel of Figure 3-3). At 900 K relatively little stress concentration remains, consistent with the total decrease in stress seen in Figure 3-2. From this stress data, it is not immediately clear what is causing the decrease in stress during the simulation, including if it is a function of structural changes in the glass. Next, we evaluate the existence of coordination defects in the glass and how their evolving concentration may act as a stress dissipation mechanism.

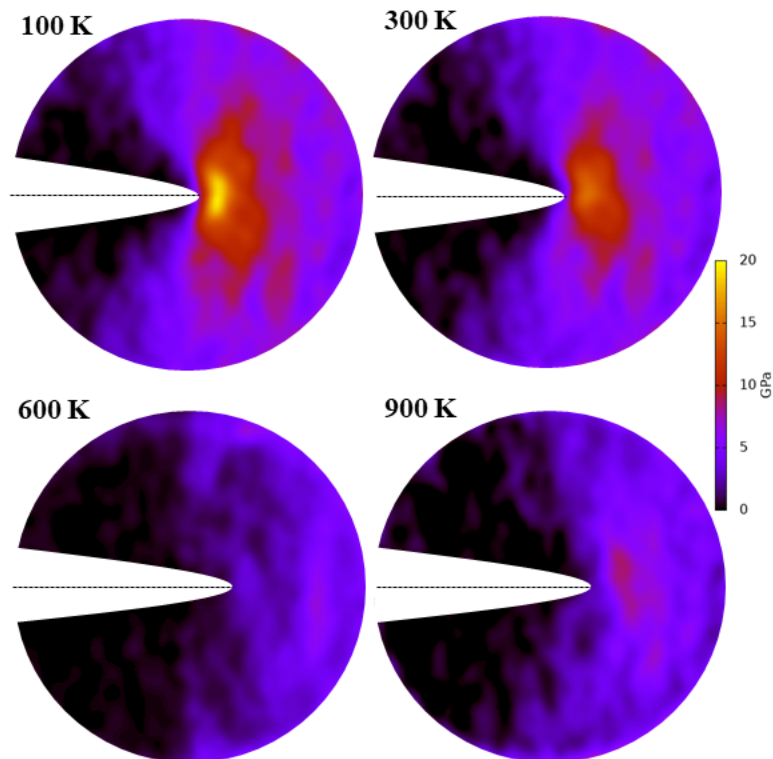


Figure 3-3: Values of per-atom virial stress (S_{YY}) distribution ahead of crack tip following relaxation at varying temperatures (100 K, 300 K, 600 K, 900 K) at the final time step of the simulation ($t = 500$ ps) centered at the final crack tip location. Data was binned spatially, averaged, and then linearly interpreted onto a grid across the four replicate structures.

It is clear that the stress field surrounding the silica crack tip exhibits a strong radial dependence, which drives structural relaxation and defect formation. By compiling the distribution of defects surrounding the crack tip we can identify if the defect concentration follows the same distribution as stress. Visual representation of the change in defect concentration following relaxation at varying temperatures is included in Figure 3-4. Note the decrease in defect concentration directly ahead of the crack tip in the 900 K simulation (bottom right, Figure 3-4) and the larger concentration of defects in the immediate vicinity of the crack tip in the 300 K and 600 K simulations. The high strain energy at the crack tip plus the addition of thermal energy is sufficient to decrease the defect concentration at the crack tip, either by removing them entirely, transforming them to other lower energy defects, or by defect migration away from the crack tip. The formation of defects due to mechanical effects, primarily compression, has been noted, with the creation of high coordination defects such as Q_5 species or over bonded oxygen being the most common.⁷⁷

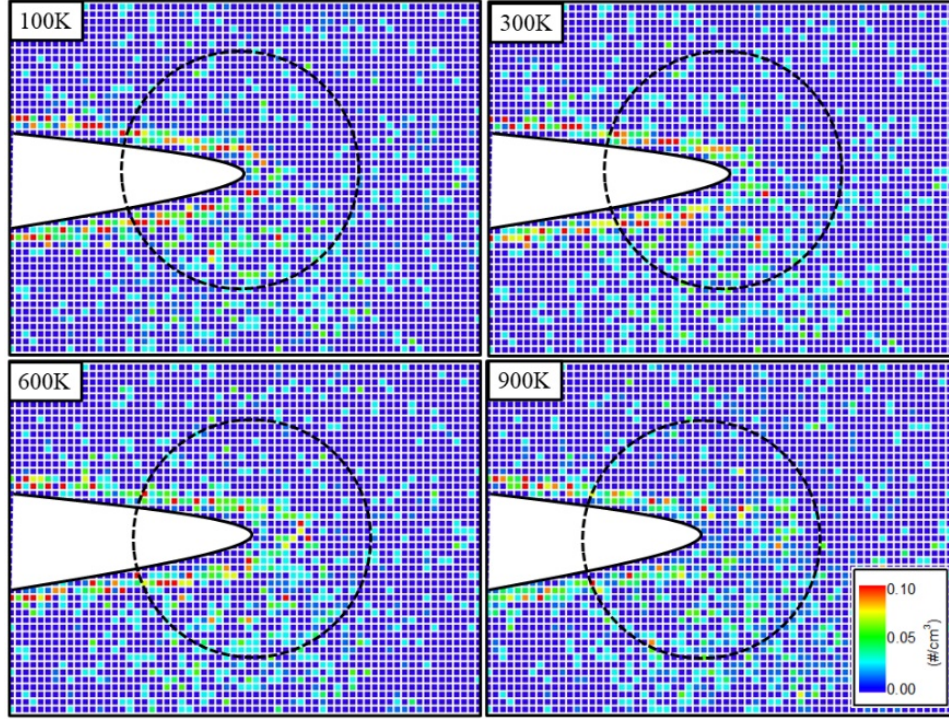


Figure 3-4: Defect density in the region surrounding the crack tip at the final time step of the relaxation ($t = 500$ ps). Blue = 0.0 defects/ cm^3 and red = 0.1 defects/ cm^3 . Defect concentration includes defects from all four replicates and centered over the final crack tip location.

To support qualitative changes in defect concentration observed in Figure 3-4, Figure 3-5 plots the concentration of defects as a function of both temperature and distance from the crack tip. The defect concentration surrounding the crack tip, prior to any structural relaxation, exhibits an inverse radial decay due to defects introduced by slit crack and the application of the stress field. The addition of the slit crack and the stress field induced by loading results in an increase of defects in the system near the crack tip, compared with an initial uniform bulk concentration of $0.0525 \text{ \#}/\text{nm}^2$ (which is approximately the far-field concentration after the slit is introduced).

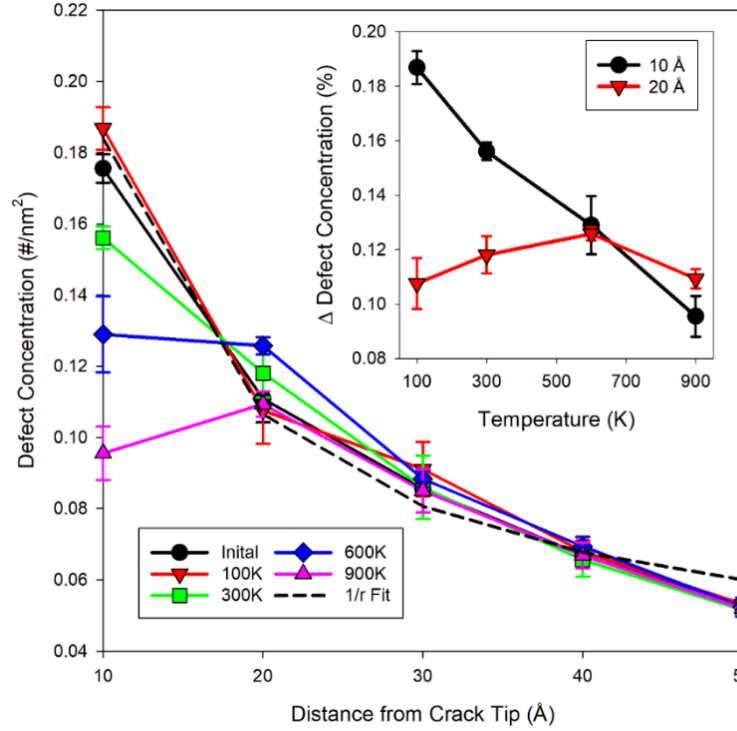


Figure 3-5: Total change in defects (%) as a function of distance from the crack tip during 500 ps of relaxation in silica glass, binned in 10 Å increments. Inset: Change in defect concentration 10 Å and 20 Å away from the crack tip as a function of temperature.

The initial defect concentration and the concentration after the 100 K relaxation follows a $1/r$ decrease that is consistent with the stress field. At temperatures 300 K and above, the defect concentration starts to diverge for the region that is less than 30 Å from the crack tip. The divergence of the defect concentration within this 30 Å region indicates that this is the size of the process zone in amorphous silica. This is consistent with previous MD studies on glass fracture, which used the convergence of the J-integral to identify the size of the process zone in the active region.³² Within the first 10 Å of the crack tip, there is a clear trend in decreasing defect concentration as a function of temperature. At 900 K, the defect concentration drops to $0.096 \pm 0.007 \text{ #/Å}^2$ from $0.175 \pm 0.006 \text{ #/Å}^2$ in the initial slitted structure. Additionally, the defect concentration decreases as the temperature increases, indicating that there is sufficient thermal energy to reduce defects in this region. At 20 Å from the crack tip there is an opposing trend, with the 600 K simulation having the highest defect concentration ($0.126 \pm 0.002 \text{ #/Å}^2$), followed by 300 K ($0.118 \pm 0.007 \text{ #/Å}^2$), 100 K ($0.111 \pm 0.007 \text{ #/Å}^2$), and then 900 K ($0.109 \pm 0.004 \text{ #/Å}^2$). The same trend is seen 30 Å from the crack tip, though the separation is less distinct. As a result, the decrease in defects within the first 10 Å appears to cause an increase in defects in the remainder of the inelastic region/process zone for the 300 K and 600 K simulations. The result is a higher defect concentration 20-40 Å from the crack tip, which can serve as a driver for the further relaxation (and crack growth) that is seen in the 900 K profile. The above results suggest that both defect creation and annihilation can be a method of decreasing the energy of the system to a more relaxed state, indicating that this is a complex multi-step phenomenon that is worthy of additional study.

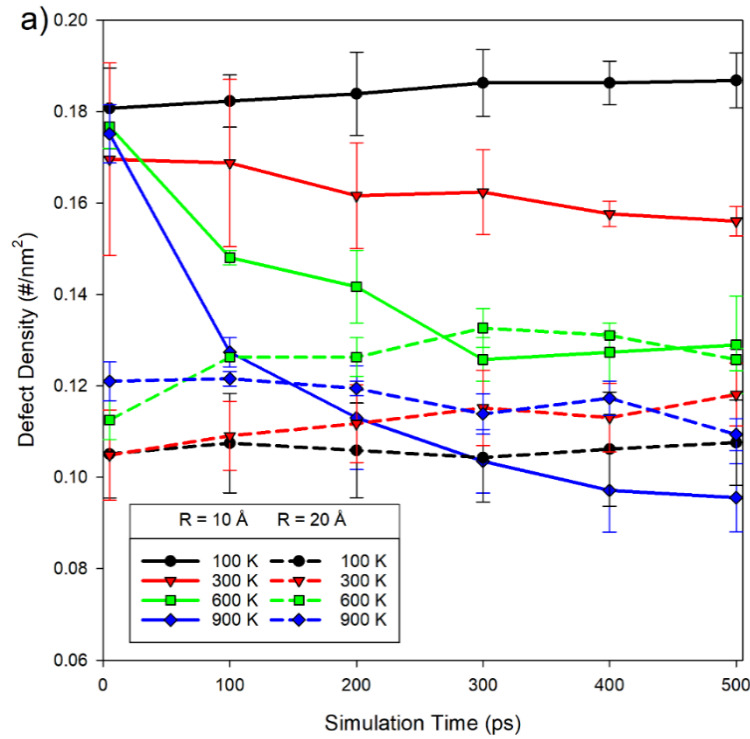
Figure 3-6.a shows how the defect density at radii of 10 Å and 20 Å evolve over simulation time while held at different temperatures. Data for 30 Å and 40 Å radii are included in Table 3-1. At

10 Å there is consistent trend of defect density decreasing with time at all temperatures except 100 K. At 20 Å there is a moderate increase in defect density at 600 K, as noted earlier. Little evolution is seen at 30 Å and 40 Å. The outermost radius of 50 Å is not included in the analysis as it is close to the rigidly deformed boundary region and so defect evolution is constrained.

In order to quantify the connection between higher temperatures and a longer simulation time we applied a TTS strategy with an Arrhenius scaling factor. The time, t , for data corresponding to temperature T is scaled by a factor of $t_{T_0} = a_T t$ where t_{T_0} is the scaled time assuming a reference temperature of T_0 and

$$\ln a_T = -\frac{E_A}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (3-2)$$

E_A is an activation energy and k is the Boltzmann constant. TTS has been previously used to identify viscoelastic effects in non-crystalline materials⁷⁸⁻⁷⁹ and is applied here as a method to estimate the time scales accessed by the elevated temperatures. Scaling the times according to Equation (3-2) an activation energy of $E_A = 0.18$ eV causes the data in Figure 3-6.a to collapse to a master defect density curve for each radius. A single activation energy is used to provide a global energy for Si-O bond breakage that covers the high temperatures and stress states generated here. This is shown in Figure 3-6.b with a reference temperature of $T_0 = 300$ K. Changing the reference temperature T_0 does not change the quality of the fit of the TTS scaling, only the magnitude of the time axis as T_0 is the temperature at which time is scaled by a factor of unity. The TTS scaling captures the monotonic decrease in density at 10 Å as well as the increase in defects at 20 Å.



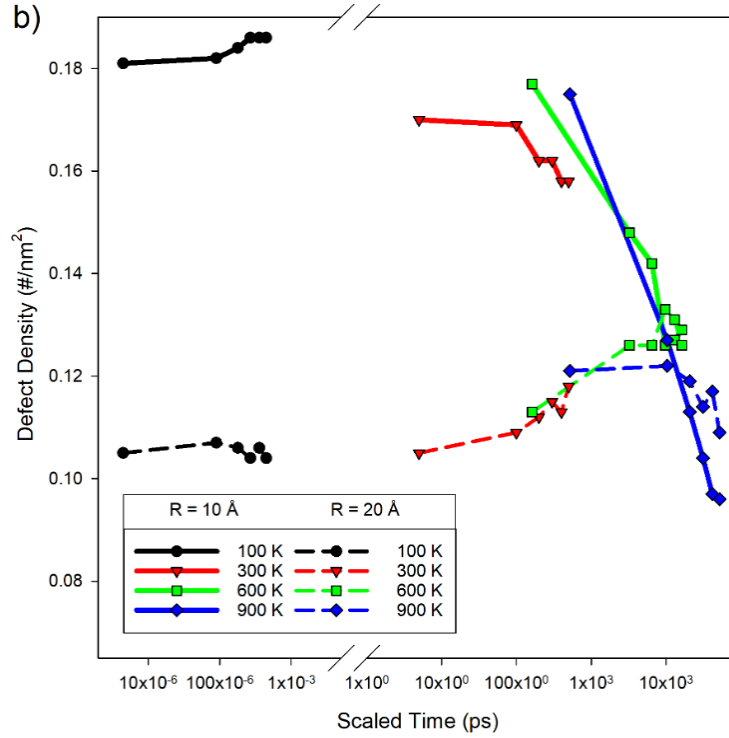


Figure 3-6: (a) Defect density evolution at 10 Å and 20 Å radius and varying with temperature and (b) defect density evolution scaled with an Arrhenius TTS strategy. For the defect density the average and the standard deviation of four different simulations are included. The data for 30 Å and 40 Å radius is included in Table 3-1.

The result is that the high temperature simulations, combined with the high stress conditions near the crack tip, are accelerating defect movement near the crack tip. Making the connection between higher temperatures and longer relaxation times, it appears that the distribution of defects initially peaks at the crack tip, diffuses away from the crack tip, and then subsides on a longer timescale. Note that we use the term diffusion in a qualitative sense, noting that the profiles look similar to diffusion equation solutions, but the underlying process may not be mechanistically diffusive and is likely stress driven.

Table 3-1: Defect density (#/nm²) with varying time and temperature for a radius (R) of 30 Å and 40 Å. Average and standard deviation of the four simulations is reported, along with the adjusted time (ps) from the Arrhenius TTS strategy.

Temp (K)		Simulation Time (ps)					
		5	100	200	300	400	500
100	R = 30 Å	0.087 ±0.005	0.086 ±0.007	0.088 ±0.008	0.087 ±0.008	0.088 ±0.008	0.091 ±0.008
	R = 40 Å	0.067 ±0.004	0.066 ±0.003	0.067 ±0.003	0.066 ±0.004	0.066 ±0.003	0.068 ±0.003
	Adj. Time	4.47x10 ⁻⁶	8.95x10 ⁻⁵	1.79x10 ⁻⁴	2.69x10 ⁻⁴	3.58x10 ⁻⁴	4.47x10 ⁻⁴

Temp (K)		Simulation Time (ps)					
300	R = 30 Å	0.083 ±0.006	0.085 ±0.007	0.086 ±0.007	0.087 ±0.007	0.087 ±0.009	0.086 ±0.009
	R = 40 Å	0.067 ±0.002	0.068 ±0.002	0.066 ±0.003	0.067 ±0.002	0.066 ±0.003	0.066 ±0.005
	Adj. Time	5.00x10 ⁰	1.00x10 ²	2.00x10 ²	3.00x10 ²	4.00x10 ²	5.00x10 ²
600	R = 30 Å	0.085 ±0.005	0.083 ±0.004	0.080 ±0.002	0.087 ±0.001	0.086 ±0.002	0.088 ±0.002
	R = 40 Å	0.066 ±0.001	0.066 ±0.003	0.070 ±0.003	0.067 ±0.001	0.070 ±0.003	0.069 ±0.003
	Adj. Time	1.63x10 ²	3.25x10 ³	6.50x10 ³	9.75x10 ³	1.30x10 ⁴	1.63x10 ⁴
900	R = 30 Å	0.088 ±0.003	0.088 ±0.003	0.082 ±0.005	0.085 ±0.003	0.085 ±0.004	0.085 ±0.006
	R = 40 Å	0.068 ±0.002	0.070 ±0.004	0.066 ±0.003	0.068 ±0.003	0.065 ±0.005	0.067 ±0.004
	Adj. Time	5.19x10 ²	1.04x10 ⁴	2.07x10 ⁴	3.11x10 ⁴	4.15x10 ⁴	5.19x10 ⁴

Some crack growth is observed during relaxation, with total crack growth between 3.9-8.8 Å. This is significantly less crack growth than previously reported for mechanical loading conditions of silica loaded up to 1.0 MPa√m.³⁰⁻³¹ Interestingly, characteristics of the crack lengths follow a non-linear trend with temperature; see data in Table 3-2. The 300 K and 600 K conditions exhibited the highest total crack growth, average fracture length per propagation event, and longest fracture per propagation event, with both 100 K and 900 K exhibiting smaller cracks and less crack growth. With the constant load, no crack healing or negative crack growth is seen in the simulations. Therefore, the 300 K and 600 K simulations exhibit both (i) increasing defects at 20 Å from the crack tip and (ii) more total crack growth. This indicates that there may be a correlation between increased defect concentration ahead of the crack tip and slow crack growth, though further studies will be required to confirm this relationship.

Table 3-2: Crack propagation data during relaxation in silica at varying temperatures. Data is the average and standard deviation of four silica glass simulations.

Temp. (K)	Total Crack Growth (Å)	Fracture Events (#)	Average Fracture Length (Å)	Longest Fracture (Å)	Change in Defects (%)
100 K	2.3±2.2	6.0±4.1	0.3±0.1	1.1±0.8	0.5±1.6
300 K	8.8±4.8	11.0±4.7	0.8±0.1	3.5±0.9	1.4±3.6
600 K	7.9±1.3	8.8±1.3	0.9±0.0	3.2±0.4	2.1±1.7
900 K	6.1±0.3	10.5±2.6	0.6±0.2	2.1±0.3	-7.0±1.1

Note: “total Crack growth” is the total distance the crack propagated; “fracture events” is the number of times that crack depth changed; “average fracture length” is how far, on average, the crack propagated during each fracture event.

Given the change in stress of the silica as a function of temperature and distance from the crack tip observed in Figure 3-2, we can identify structural differences and defect distribution in the silica that caused the change in stress. Evaluation of changes in the local structure of the silica glass, such as Si-O bond distances indicates that average structure did not change significantly during relaxation. Therefore, we have undertaken a defect analysis of the silica glass to identify which coordination defects, if any, are formed or removed during relaxation. The analysis considers bonding defects, such as Si^3 , Si^2 , or NBO, and differences in number of BO per silica, such as Q_3 , Q_2 , and Q_1 structures. Finally, the parametrization of ReaxFF used here has been known to generate over coordinated silicon and oxygen defects ⁶² and both of these defects are included in the analysis.

Overall, the 900 K simulations exhibit the sharpest decrease in total defect concentration, losing nearly 7.0% of the defects over the course of the simulation; see Table 3-2. The decrease in defects at 900 K is expected due to the relatively high temperature, allowing for defects to be annealed out of the structure. Conversely, the 100 K, 300 K and 600 K simulations have a very small net gain in defect concentration during relaxation of between 0.5-2.0 %.

The MD simulations that were performed identified which defects are formed and removed during relaxation of a slit crack in silica due to stress relaxation mechanisms and annealing. The highest energy defects are most likely to be removed during relaxation, and high concentration of defects may serve as sites for crack growth and also drive migration. Figure 3-7 and Table 3-3 include a breakdown of the change in defect concentration at varying temperatures.

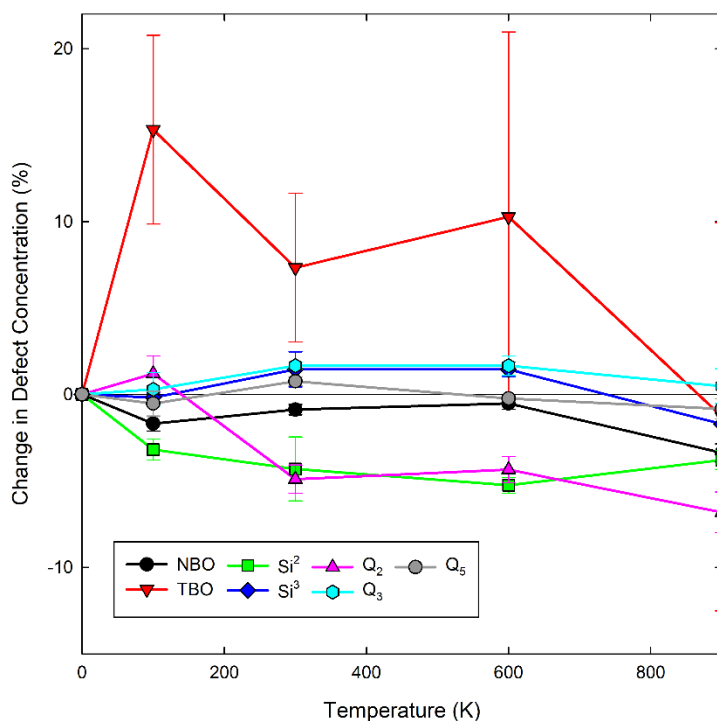


Figure 3-7: Total change in defect concentration (%) after relaxation of silica at four different temperatures (100 K, 300 K, 600 K, 900 K). The average and standard error of four replicates is reported.

Table 3-3: Change in coordination defect concentration in silica following relaxation separated by defect type and temperature. Average of four replicates is reported along with the standard error.

Temp (K)	NBO	TBO	Si ²	Si ³	Q ₁	Q ₂	Q ₃	Q ₅
100	-0.86 ±0.47	23.94 ±12.38	-8.90 ±0.33	-2.87 ±0.044	-8.33 ±8.33	3.71 ±6.15	0.92 ±0.23	0.23 ±0.25
300	-0.88 ±0.30	7.34 ±4.30	-4.31 ±1.85	1.45 ±1.02	-9.09 ±4.55	-4.90 ±0.82	1.67 ±0.19	0.76 ±0.25
600	-0.52 ±0.35	10.28 ±10.69	-5.25 ±0.46	1.45 ±0.42	-	-4.35 ±0.75	1.67 ±0.57	-0.23 ±0.17
900	-3.38 ±0.52	-1.28 ±11.23	-3.79 ±0.55	-1.71 ±0.12	-	-6.82 ±1.18	0.48 ±1.00	-0.84 ±0.58

Positive values in Table 3-3 indicate a net increase in defects during relaxation. Across all the conditions evaluated, NBO and Si² defects are removed consistently, while the Q₃ defect concentration increases. The decrease in NBO and Si² arise from forming bonds in a Q₃-Si³ or related pair of defects (Q₃-Q₃, Si²-Si³, Q₄-Q₃, etc.). A single bond formation event between a Q₂ and a Si² species results in formation of a Q₃ bound to a Si³ species, consistent with the trends noted above. As illustrated in Figure 3-8, a representative defect balance is:



Therefore, the silica linkages containing Si² and Q₂ species are some of the most reactive defects in the system since they are removed the most quickly during relaxation of the silica. Interestingly, TBO are also formed in low concentrations, and have been reported in previous ReaxFF simulations, but are seldom seen in experimental glass structures. At 100 K an increase in TBO defects of nearly 24% occurred. In comparison, there is an increase of 7% TBO defects at 300K and 10% at 600 K. At 900 K the amount of TBO decreases, indicating that at sufficiently high temperatures defects are removed, rather than being formed. Typically, TBO are formed in silica undergoing nanoindentation, as a temporary structure due to an uncoordinated silicon atom being coordinated by a BO atom.⁷⁷ The main difference here is that during the previous reports of nanoindentation the high coordination defects were no longer present once these loading was removed.^{77, 80-81} In these simulations, stress relaxation is responsible for the structural relaxation, which may indicate that the ability of the TBO to be removed is a function of a stress mediated mechanism.

Other defects including Q₁, Q₂, and Q₅ species have behavior that is less clearly monotonic with temperature. Overall, higher coordination defects are formed at the expense of lower coordination defects (Q₃ v. Q₂, Si³ v. Si², TBO v. NBO). The formation and removal of defect species during relaxation indicates that the drive to relax the structure is capable of significant defect formation, which can aid in slow crack growth at nanoscale levels.

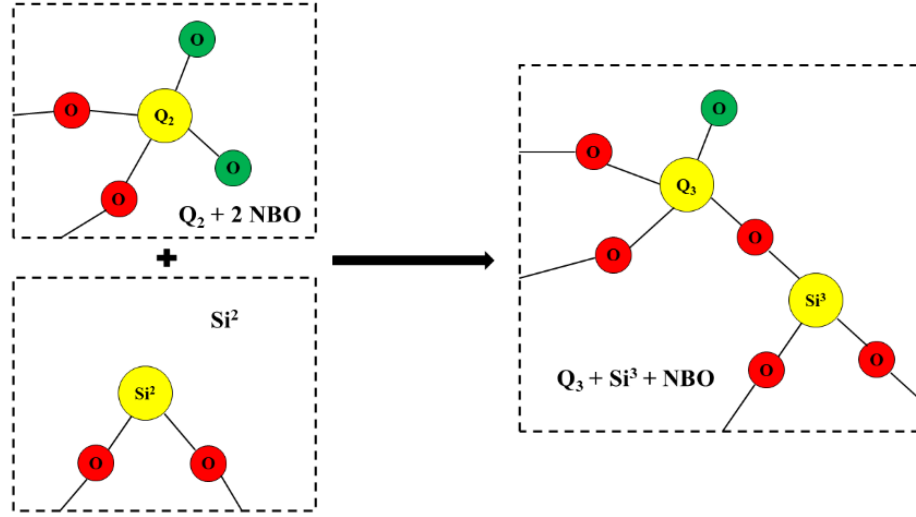


Figure 3-8: Schematic of formation of a Q_3 - Si^3 linkage due to the removal of Si^2 , Q_2 , and NBO defects. Colors: Si (yellow), BO (red), NBO (green)

3.5. Conclusions

Inelastic relaxation of silica glass in the vicinity of a crack tip was explored via reactive MD simulations. A slit crack was introduced into silica structure models, loaded with far-field displacements consistent with an analytical elasticity solution, then relaxed at four temperatures (100 K, 300 K, 600 K, 900 K). The highest stress dissipation occurred at 900 K and was most concentrated within 10 Å from the crack tip. At distances greater than 30 Å there were limited changes in stress, indicating that the inelastic region was restricted to within 30 Å from the crack tip. The stress concentration was also related to the defect concentration, with the higher stress sustained in the 100 K simulation also resulting in a higher defect concentration at the crack tip (0.18 #/nm²) after inelastic relaxation. In comparison, at 900 K the defect concentration at the crack tip dropped significantly, to 0.09 #/nm², which also corresponded to a decrease in stress. At 20 Å from the crack tip a defect enriched region was formed, with an increase in defect concentration for the 100 K, 300 K, and 600 K simulations. It was theorized that the increase in defect concentration in the 20 Å region is due to a defect migration mechanism, where defects move away from the crack tip due to structural relaxation. Analysis of the defect speciation identified that the decreases in defect concentration was due to removal of undercoordinated silica defects, such as NBO and Si^2 species, and the formation of Q^3 and Si^3 , so that the trend is toward higher average silicon and oxygen coordination. Overall, stress relaxation causes the formation and removal of defects from the inelastic region, which is temperature dependent, and may factor in fracture growth at an atomistic level.

4. SODIUM MIGRATION DURING SILICA FRACTURE

4.1. Overview

Reactive classical MD simulations of sodium silicate glasses, $x\text{Na}_2\text{O}-(100-x)\text{SiO}_2$ ($x=10-30$), under quasi-static loading were performed for analysis of molecular scale fracture mechanisms. Mechanical properties of the sodium silicate glasses were consistent with experimental reported values, and the amount of crack propagation varied linearly with reported fracture toughness values. The most crack propagation occurred in NS20 systems (20 mole % Na_2O) compared with the other simulated compositions. Dissipation via two mechanisms, the first through sodium migration as a lower activation energy process, and the second through structural rearrangement as a higher activation energy process, was calculated and accounted for all the energy that was not stored elastically or associated with formation of new surfaces due to crack propagation. A correlation between crack propagation and energy dissipation was identified, with systems with higher crack propagation exhibiting less energy dissipation. Sodium silicate glass compositions with lower energy dissipation also exhibited the most sodium movement and structural rearrangement within 10 Å of the crack tip during loading. Therefore, high sodium mobility near the crack tip may enable energy dissipation without requiring defect formation in the silica network. These results highlight that the varying mobility of the network modifiers near crack tips influence the brittleness and the crack growth rate of modified amorphous oxide systems. This chapter is adapted from the following publication: Rimsza, Jessica M., and Reese E. Jones. "Fracture mechanisms of sodium silicate glasses." *International Journal of Applied Glass Science* (2022). (doi.org/10.1111/ijag.16594)

4.2. Introduction

Oxide glasses are a common brittle material and are widely used in optics⁸², microelectronics⁸³, and in structural materials⁸⁴. These materials primarily exhibit brittle fracture, causing sudden and unanticipated failures that result in reliability concerns. As a result, research has focused on the different fracture mechanisms that can occur in amorphous systems and how they impact the long-term behavior of glasses.

Past analysis of fracture in amorphous oxides has noted the existence of an inelastic region surrounding the crack tip, which has higher reactivity and differing relaxation properties than regions farther from the crack tip.^{32, 40} Generally, this inelastic region only extends a few nanometers from the crack tip.^{18, 30-31} Therefore, recently developed molecular scale simulation methods have demonstrated the ability to evaluate the unique structure and mechanisms that occur in this inelastic region and can impact fracture.^{18, 30-32, 40, 44, 85} Thus far, this analysis has primarily focused on pure silica glasses loaded in tension, which has been shown to introduce voids ahead of the crack tip or extending from points of high stress in the geometry.^{48-52, 86-88} The results have been successful in identifying how the glass structure responds to strain and the mechanisms that result in void formation and fracturing. Computational evaluation of the fracture mechanisms of multicomponent amorphous oxides are rare, but both sodium silicate glasses⁸⁹ and calcium-silicate-hydrates⁹⁰⁻⁹² have been evaluated for their fracture properties in tension. The results from these studies suggest that the presence of modifiers can adsorb the stresses caused by mechanical deformation.

It is critical to understand fracture mechanisms beyond just pure silica glasses, since they are relatively uncommon in industrial applications. Further, the inclusion of modifiers in the silica network significantly changes the structure-property relationships that control the resulting macroscopic properties. Sodium silicate glasses constitute one of the simplest glass compositions that can be used for evaluation of the role of modifiers on fracture properties. The structure of sodium silicate glasses

has been extensively evaluated both experimentally⁹³⁻⁹⁷ and computationally⁹⁸⁻¹⁰⁴. These studies ascertained that the introduction of sodium breaks up the silica network and alters the intermediate range structure. The change in the structure causes decreasing strength with increasing sodium concentration.¹⁰⁵

Despite extensive investigations on the role of sodium in altering the structure of the silica glass, as well as the impact of sodium on mechanical properties and fracture under tension, it is still unclear how sodium atoms within the inelastic zone are controlling the fracture properties of sodium silicate glasses. Therefore, we have applied the recently developed Na/Si/O/H reactive forcefield ReaxFF¹⁰⁶ to perform classical MD modeling of fracture in sodium silicate glass compositions (10-30 mole %) under far-field mode I conditions where the crack is loaded primarily in tension. Energy dissipation, sodium and silicon movement, and evolution of defect structures are analyzed for their role in inhibiting fracture propagation in sodium silicate glass compositions.

4.3. Computational Methods

The classical MD simulations in this study were performed using a reactive force field⁵⁸⁻⁵⁹, which has been parametrized for sodium silicate glasses.⁶⁰ ReaxFF allows for bond breakage and formation, which is necessary for classical MD simulations that include reactive species, such as water,⁶¹⁻⁶³ or when bond breakage is expected, such as during fracture.^{31, 41} Thin, quasi-2D simulation cells (150 Å x 150 Å x 25 Å) of sodium silicate glasses were created through a melt-and-quench procedure. Deng et al.¹⁰⁷ performed an exhaustive evaluation of protocols for generating sodium silicate glasses using several different forcefields, including Teeter¹⁶, a ReaxFF version used by Yu et al.¹⁰⁸, and the Na/Si/O ReaxFF forcefield used here.⁶⁰ Based on these results, we employed a less computationally expensive Pedone forcefield¹⁰⁶ in an initial melt and quench procedure, that resulted in experimentally validated structural and mechanical properties of a variety of modified glass structures. To start, a simulation box with a mixture of Na, Si, and O atoms for the specific glass composition of interest (see Table 4-1) was generated with random atomic positions. The melt and quench protocol began with heating the simulation box to 3500 K at a rate of 100 K/ps, holding the simulation at 3500 K for 100 ps, and then cooling to 300 K at a rate of 5 K/ps. A final 100 ps equilibration at 300 K was performed. All simulations used a NPT ensemble with a 1.0 fs time step damping parameter equal to 100 time steps for the thermostat and 1000 time steps for the barostat. Following the melt and quench with the Pedone forcefield, an annealing step with the Na/Si/O ReaxFF forcefield was performed. Using a 0.25 fs time step, the sodium silicate glasses were heated from 300 K to 1500 K at a rate of 5 K/ps, held at 1500 K for 80 ps, and cooled at a rate of 5 K/ps back to 300 K. The annealing procedure used an NPT ensemble as well, with a damping parameter equal to 100 time steps for the thermostat and 1000 time steps for the barostat. A final equilibration was performed in an NVT ensemble for 10 ps with a 0.25 fs time step. This procedure generated the structures used in the fracture simulations. Data on the structural features of the bulk sodium silicate glasses are including in Figure 4-1. All simulations were performed using the LAMMPS MD code with the USER-REAXC package.¹⁰⁹

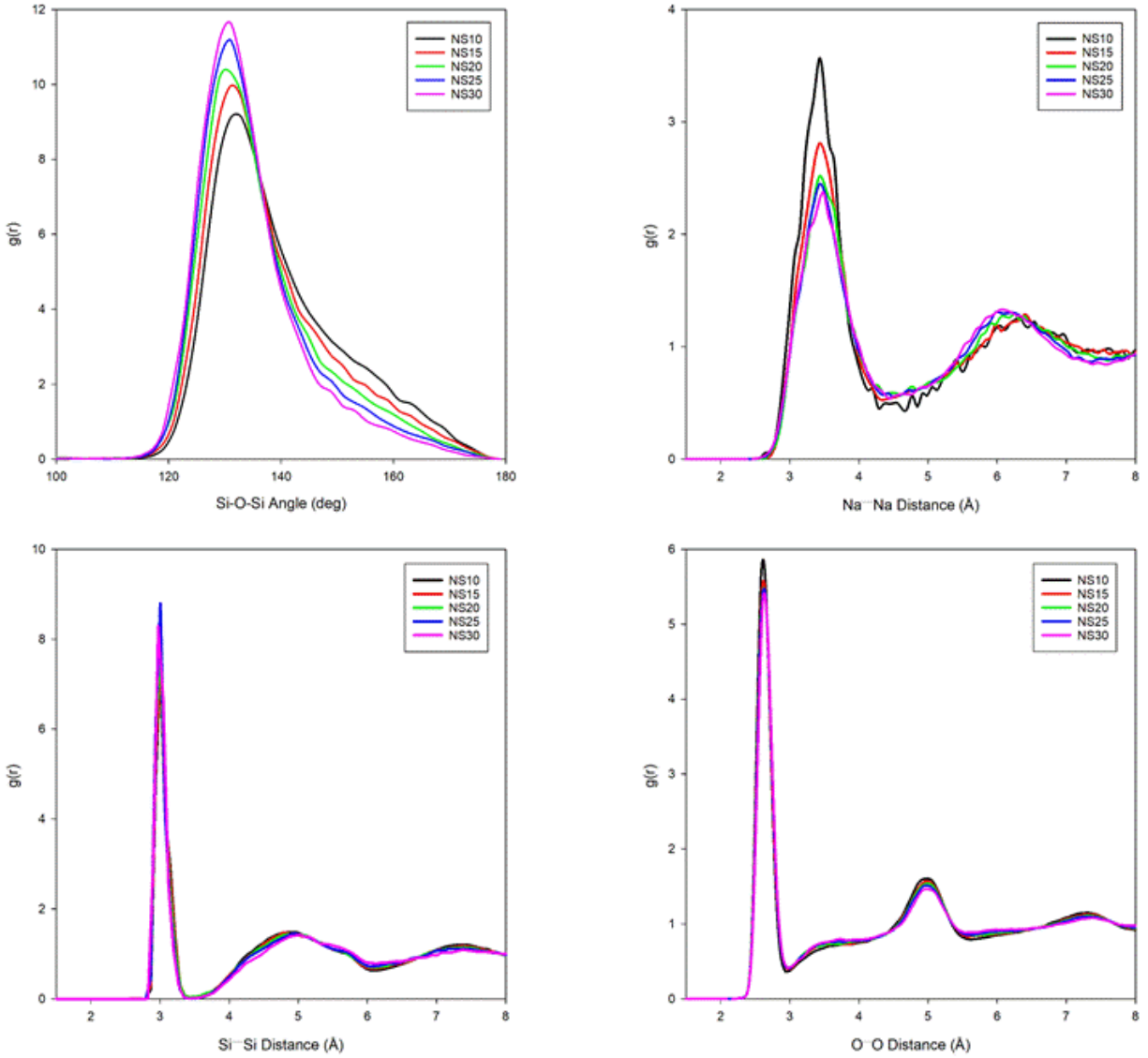


Figure 4-1: (upper left) Si-O-Si bond angle distribution data for sodium silicate glasses with varying sodium concentrations, (upper right) Na-Na pair distribution function for bulk sodium silicate glass with varying sodium concentration. Note that the smoothness of the PDF increases with increasing sodium concentration, (bottom left) Si-Si pair distribution function for bulk sodium silicate glass with varying sodium concentration (bottom right) O-O pair distribution function for bulk sodium silicate glass with varying sodium concentration

For evaluation of inelastic relaxation, a perfect slit crack was created in the sodium silicate glass by removing interactions between upper and lower sets of atoms separated by a plane extending halfway into the system (see Figure 4-2.a). To sample the isotropy expected in the amorphous systems, the original silica model was rotated by 90° three times and a slit crack was introduced into the same half plane to create four distinct systems. The average and standard error of the four simulations are reported throughout the manuscript.

The crack was mechanically loaded by displacement of far-field atoms in a region outside a cylinder centered on the crack tip (see Figure 4-2.a). The active region has a radius of 6.5 nm. While

the amorphous systems studied here are not identical to ductile metals, similar mechanisms of crack tip blunting do occur and predicted process zones are expected to fall within the size of the active region. The atoms with prescribed displacement are fixed to maintain the loading over the course of the simulation. The displacement field (u_1, u_2) was taken from the classical LEFM continuum solution for a semi-infinite slit crack in mode I loading⁶⁹ in Equation 4-1.a and 4-1.b:

$$u_1 = \frac{K_I}{2G\sqrt{2\pi}} \cos\left(\frac{\theta}{2}\right) \left[k - 1 + 2\sin^2\left(\frac{\theta}{2}\right) \right] \quad (4-1.a)$$

$$u_2 = \frac{K_I}{2G\sqrt{2\pi}} \sin\left(\frac{\theta}{2}\right) \left[k + 1 - 2\cos^2\left(\frac{\theta}{2}\right) \right] \quad (4-1.b)$$

The displacement field is spatially varying (r, θ are polar coordinates) and is parameterized by the stress intensity factor K_I ($k=3-4$ ν depends on the Poisson's ratio ν of the material). The result is a prescribed displacement for each boundary atom that is a function of the atom's distance from the crack tip. Figure 4-2.b shows the radial displacement field of the system at $K_I = 1.2 \text{ MPa}\sqrt{\text{m}}$ of loading which seamlessly blends with the prescribed boundary displacements. Under this loading, the slit crack develops a stress singularity that is characteristic of all classical cracks prior to relaxation,⁷⁰ which is distinct from notch geometries.⁷¹⁻⁷² G and ν that were used to construct the far-field plane strain mode I loading were calculated and reported in Table 4-2.

The crack was first opened in one step to a K_I value of $2 \times 10^{-2} \text{ MPa}\sqrt{\text{m}}$ via the prescribed displacement field. Following crack opening, the interior active region was relaxed with the exterior region fixed. Then alternating minimizations and low-temperature NPT relaxations were performed to reach a relaxed structure through a sequence of K_I increments. Loading was accomplished by simulating the system for 5 ps then increasing the loading by $0.01 \text{ MPa}\sqrt{\text{m}}$ in a form of quasi-static loading. This process was repeated up to a final loading state of $1.2 \text{ MPa}\sqrt{\text{m}}$. The system temperature was controlled at 300 K with a Langevin thermostat throughout.

To assess the various compositions and parameterize the K_I loading, elastic constants were calculated for the final sodium silicate glass structures, prior to introducing the slits, by performing negative and positive box displacements in the x-, y-, and z-dimensions. The resulting stresses were used to compute the elastic stiffness tensor. A relatively large displacement of 1% was used, based on a convergence study of displacement versus mechanical properties. K , E , G , and ν , were calculated using the estimated elastic stiffness tensor. Surface energies were calculated from the same final sodium silicate glass structures, with the addition of 50 Å of vacuum space inserted into the simulation cell in the x-, y-, or z-dimension. Following the creation of the surfaces the system underwent minimal relaxation for 10 ps at 0.1 K in an NVT ensemble. The final energy of the bulk silica (E_{bulk}) following the same relaxation procedure, the energy of the silica with the surfaces (E_{surface}) and S_A are used to calculate γ :

$$\gamma = \frac{E_{\text{surface}} - E_{\text{bulk}}}{2S_A} \quad (4-2)$$

Here, a shorter relaxation scheme is used for calculation of the surface energy to capture an unannealed surface energy value that is more consistent with a fracture surface energy⁷⁴, than a fully annealed or hydroxylated silica surface.

Table 4-1: Composition and density of sodium silicate glass and comparison with experiment

Composition (atoms)				Density (g/cm ³)	
	Na	Si	O	This Work	Ref: ¹¹⁰

	Composition (atoms)			Density (g/cm ³)	
NS10	2550	11525	24325	2.42	2.30
NS15	3850	10875	23675	2.44	2.34
NS20	5100	10250	23050	2.45	2.38
NS25	6400	9600	22400	2.46	2.43
NS30	7700	8950	21750	2.46	2.47

Table 4-2: Young's (E) and shear (G) modulus and surface energy for sodium silicate glass and comparison with experiment.

	E (GPa)		G (GPa)		ν	Surface Energy (J/m ²)
	This Work	Ref ¹⁰⁵	This Work	Ref ¹⁰⁵	This Work	This Work
NS10	82.7	73.4	32.6	29.9	0.27	1.74
NS15	74.9	65.1	29.2	29.2	0.29	1.53
NS20	67.1	59.9	25.7	25.4	0.30	1.27
NS25	68.3	59.7	26.1	24.3	0.31	1.37
NS30	64.5	59.0	24.1	23.3	0.34	1.26

Overall, the mechanical properties are slightly higher than values reported from previous experimental and computational studies,¹⁰⁵ with the largest variation occurring at higher sodium concentrations. The density values are also slightly high, with the best match between experiment and computational results occurring in the NS30 sample. In the original parametrization of the Na/Si/O ReaxFF forcefield used here, only the density of the NS30 composition was used in the parametrization, which may be the cause for the differences at lower sodium concentrations.⁶⁰ Most critically, the trend between sodium concentration and the mechanical properties is consistent with experimental results, including decreasing E and G of the material with increasing sodium content.

Defect structures in the fracture simulations were identified through the evaluation of interatomic distances, using a 2.25 Å cut-off for Si-O distances, which has been previously used in MD simulations of silica using a ReaxFF force field as the first minimum in the Si-O pair distribution function.^{32, 74} An ideal oxygen atom would be bound to two silicon atoms, and a silicon atom would be bound to four BO atoms. Alternative coordination structures, such as an oxygen atom bound to only one silicon or a silicon bound to three BOs and one NBO are classified as defects and are discussed later in the manuscript.

The crack length was defined based on the atom density of the quasi-2D system calculated on a rectangular grid with spacing 1 Å spacing in x and y. The algorithm identifies the vacuum-sodium silicate edge in the simulation as where the atom density goes from zero to greater than zero. The location of the edge of the sodium silicate structure is fit to a parabola, and the crack depth is defined as the change in the location of the vertex from the initial step to the selected loading step. This method identifies overall changes in the length of the empty space that defines the interior of the crack, rather than using other recently reported methods based on the observed displacements and the stress intensity factor.⁷⁵

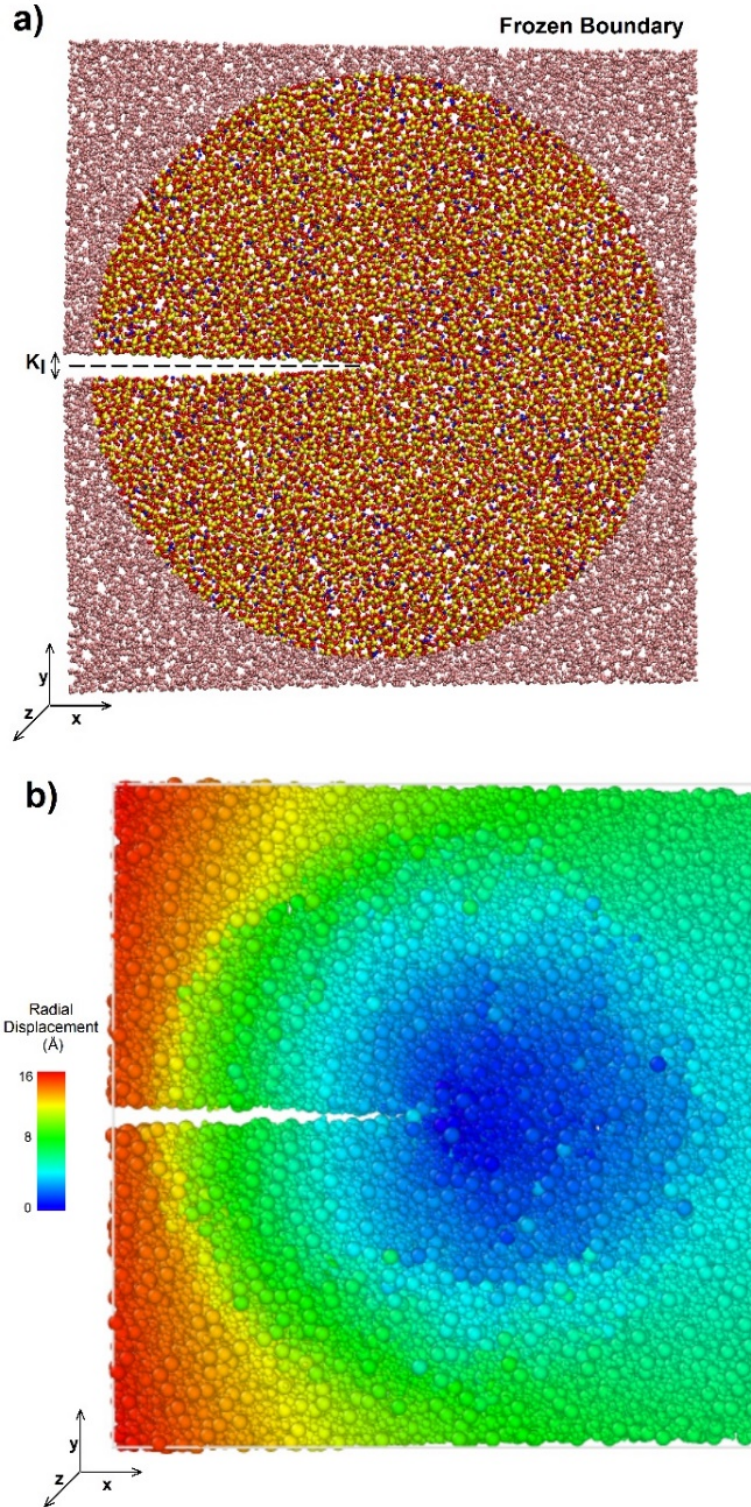


Figure 4-2: (a) Snapshot of the NS10 sodium silicate glass structure with a loaded slit crack. The half plane where the bonds are broken is included as a dashed line. The frozen boundary is where the atoms are fixed to impose the external boundary conditions (pink). Atom colors: Si (yellow), O (red), Na (blue). (b) Radial displacement field from far-field loading conditions in NS10 sodium silicate glass structure.

4.4. Results

During the quasi-static loading of the glass systems crack propagation occurs through a series of crack propagation events followed by arrests, which results in a change in the crack length. Table 4-3 includes data on the evolution of the crack, including the total crack growth, number of fracture events, the average fracture length, and the longest fracture event. While there is significant noise in the data, there is a peak in the amount of crack growth for the NS20 composition, with decreasing amounts of crack growth for lower and higher sodium concentrations. Previous experimental work by Vernaz et al. evaluated fracture toughness in sodium silicate glass compositions via a notched beam technique and identified that a NS20 glass composition had the lowest fracture toughness ($0.84 \text{ MPa}\sqrt{\text{m}}$).¹¹¹ Therefore, the same NS20 composition is expected to have the most crack growth as seen here. It is worth noting that there have been conflicting reports of the effect of sodium concentration on the mechanical properties of sodium silicate glasses.¹¹⁰⁻¹¹² For instance, Smedskjaer and Bauchy identified slower crack velocities for a NS23 composition ($5 \times 10^{-10} \text{ m/s}$) than for a NS15 compositions ($9.2 \times 10^{-10} \text{ m/s}$) following Vickers indentation.¹¹² Additionally, evaluation of failure strain in sodium silicate glass fibers identified a roughly linear relationship between mole fraction sodium to failure strain in a two-point bend test.¹¹⁰ The differences are expected to arise from the unique loading geometries used in each study (notched beams, indentation, and fibers). Here, the mode I far-field loading condition is most consistent with notched beam technique by Vernaz et al.,¹¹¹ and our data is most consistent with this experimental result.

Table 4-3: Crack propagation data during quasi-static loading of sodium silicate glasses at $0.5 \text{ MPa}\sqrt{\text{m}}$ and $1.2 \text{ MPa}\sqrt{\text{m}}$.

	Loading ($\text{MPa}\sqrt{\text{m}}$)	Total Crack Growth ($\text{\AA}$)	Fracture Events (#)	Average Fracture Length ($\text{\AA}$)	Longest Fracture ($\text{\AA}$)
NS10	0.5	0.97 ± 1.25	2.50 ± 1.80	0.31 ± 0.42	0.70 ± 1.04
	1.2	4.60 ± 0.82	7.00 ± 2.92	0.71 ± 0.13	2.87 ± 0.84
NS15	0.5	0.05 ± 0.09	0.50 ± 0.87	0.02 ± 0.04	0.02 ± 0.04
	1.2	3.95 ± 0.74	3.50 ± 1.50	1.27 ± 0.37	3.57 ± 0.66
NS20	0.5	1.52 ± 1.20	2.50 ± 1.66	0.74 ± 0.59	1.25 ± 1.14
	1.2	7.02 ± 1.51	10.25 ± 4.44	0.78 ± 0.29	2.60 ± 0.46
NS25	0.5	1.12 ± 1.57	1.00 ± 1.00	0.09 ± 0.15	1.05 ± 1.54
	1.2	5.67 ± 2.51	8.50 ± 2.06	0.65 ± 0.19	2.70 ± 0.93
NS30	0.5	0.35 ± 0.21	1.50 ± 1.50	0.27 ± 0.23	0.27 ± 0.23
	1.2	3.15 ± 1.42	5.25 ± 1.48	0.70 ± 0.38	2.00 ± 0.98

Note: “total Crack growth” is the total distance the crack propagated; “fracture events” is the number of times that crack depth changed; “average fracture length” is how far, on average, the crack propagated during each fracture event.

The results in Table 4-3 indicate that the longer crack growth in the NS20 sample arises from a higher number of fracture events (10.25 ± 4.44) than the other sodium silicate glass compositions. More frequent fracture events may indicate a lack of alternative stress dissipation mechanisms that results in increased brittleness at the crack tip and therefore more total fracture growth. The energy balance in the system includes the internal energy of the system (U) and the energy of the added

surface area (U_s), as well as the stored elastic energy and the work done on the system. The added U_s due to fracture in a quasi-2D system is equal to the change in crack length (c) multiplied by γ . Another energy term, which we define as G_{DISS} , contains all the additional dissipation effects that do not result from the formation of surface area (S_A):

$$\Delta U - \Delta U_s = - (G_{DISS} + 2\gamma)\Delta c \quad (4-3)$$

A perfectly brittle material would have a G_{DISS} value of zero, as all the stored energy lost by the material would be converted into additional surface energy.

Accounting for the system cell depth in the out-of-plane dimension results in G_{DISS} in terms of the change in internal energy (ΔU) divided by the change in the surface area (ΔS_A).

$$G_{DISS} = \frac{\Delta U}{\Delta S_A} \quad (4-4)$$

We previously derived this relationship and applied it to ReaxFF simulations of silica.³² The change in surface area ΔS_A was calculated through the construction of a surface mesh along the crack face with the Ovito Visualization Tool, with a spherical probe particle with a 3.5 Å radius. A radius of 3.5 Å allowed for calculation of the added surface area in the narrow crack without sampling the voids within the sodium silicate structure.¹¹³

The resulting G_{DISS} values are included in Figure 4-3 and identify that G_{DISS} increases up to a K_I loading of ~ 0.7 MPa $\sqrt{m}$ before leveling off. After 0.7 MPa $\sqrt{m}$ all the systems have experienced some fracture, and the evaluation of the dissipation energy becomes more complex due to addition of varying amounts of S_A and the amount of surface relaxation. Interestingly, the lower sodium compositions (NS10, NS15) appear to have a continuously increasing G_{DISS} value, even after 0.5 MPa $\sqrt{m}$, compared with G_{DISS} for higher sodium compositions (NS20, NS25, NS30) that appear to level off. The change in the trend may be an indication of the rate of inelastic relaxation, and that systems with higher sodium concentration relax faster than those with lower sodium concentration.

Prior to fracturing, at $K_I = 0.5$ MPa $\sqrt{m}$, the G_{DISS} values follow the trend NS10 > NS30 > NS25 > NS15 > NS10, which does not exhibit a linear compositional dependence. The G_{DISS} trend is consistent with the total amount of fracture, with system that exhibit highest fracture (NS20) having lower G_{DISS} values than those that exhibit less fracture (NS10/NS30); see the relationship in Figure 4-4. After 0.5 MPa $\sqrt{m}$ there is a stronger linear trend with composition with increasing decreasing G_{DISS} with compositions: NS10 > NS30 > NS15 > NS20 > NS25. Only the NS30 composition exhibits higher G_{DISS} values than expected. We believe this is due to a change in energy dissipation mechanisms, which is discussed later in the manuscript.

Overall, the energy dissipation in these sodium silicate glasses is tied to their fracture properties, with lower energy dissipation resulting in faster crack growth as would be expected for brittle materials. In the next sections we analyze the sodium silicate glass structures to identify sources of differences in energy dissipation and crack propagation between these glass compositions.

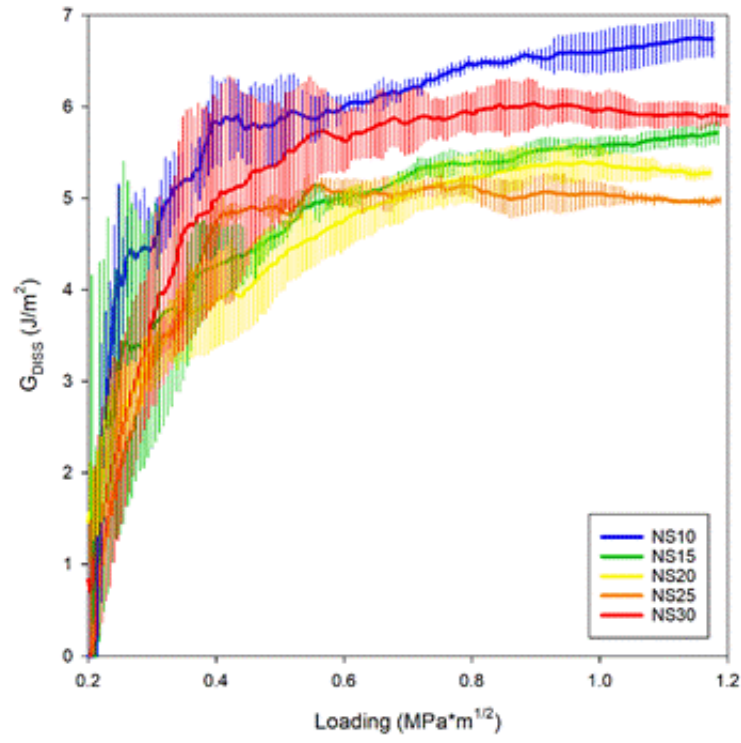


Figure 4-3: Dissipation energy (G_{DISS}) during loading of sodium silicate glasses calculated from Equation 4-4.

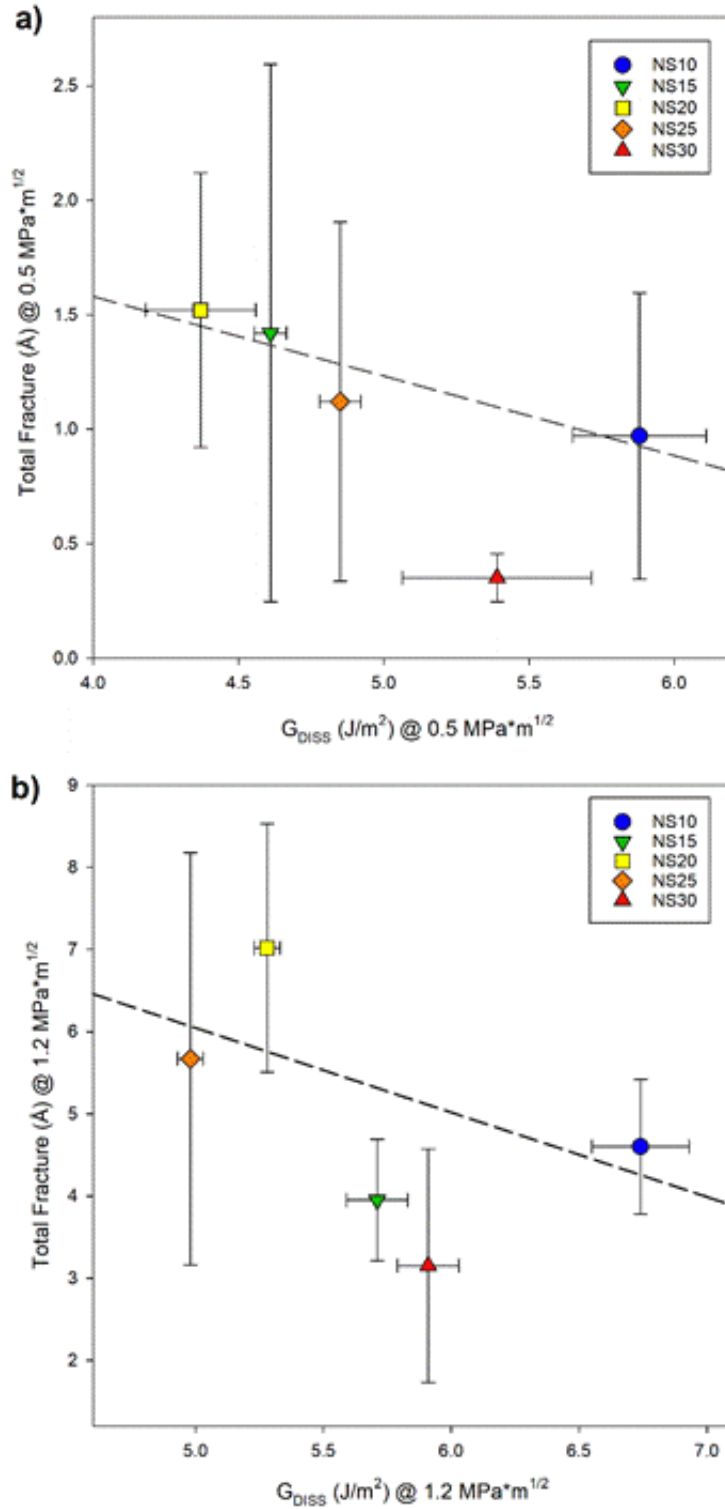


Figure 4-4: G_{DISS} and total fracture growth at (a) 0.5 MPa $\sqrt{m}$ and (b) 1.2 MPa $\sqrt{m}$ for sodium silicate glass compositions.

Observation of the sodium silicate glass structures during fracture identified significant amounts of sodium movement. We quantified this sodium movement over the entire simulation to

identify the compositional influence. The analysis is based on the initial and final position of each atom in the simulation between loading states, which is calculated via a simple distance formula and then averaged by atom type. The result is the average displacement of the atom. Additionally, the simulation temperature was maintained at a modest 300 K limiting thermal effects and the resulting sodium diffusion.

Figure 4-5.a. includes the total sodium movement during loading. As expected, the farther from the crack tip the more movement is observed based on the application of the mode I displacement field. At the crack tip, the amount of sodium movement starts to diverge, with lower and higher sodium concentration glasses (NS10, NS15, and NS30) exhibiting the least amount of sodium movement near the crack tip, while intermediate concentrations (NS20 and NS25) have the most movement (see inset in Figure 4-5.a.). The deviation from the expected trend indicates that the sodium is lagging behind the far-field loading. Increased movement in this region with 10 Å from the crack tip suggest that the region is most reactive in the NS20 and NS25 compositions.

The silicon movement is expected to be more consistent with the applied K-field loading displacement due to the higher coordination states in the interconnected silica network. Overall, silicon movement shows some similar trends (Figure 4-5.b.) to sodium displacement, with more movement farther from the crack tip than for sodium. Despite the network structure, near the crack tip there is some deviation of silicon movement as a function of composition. While NS10 and NS15 exhibit lower amounts of sodium movement (~ 1.4 Å) at higher sodium concentrations the silicon movement is elevated, ~ 2.0 Å for NS20 and NS25 and ~ 1.6 Å for NS30. The elevated silicon movement for NS20 and NS25 is expected, due to the larger crack propagation distances and higher sodium movement indicating an overall higher reactivity. The NS30 structure has the least amount of crack propagation, but still exhibits an elevated silicon movement relative to NS10 and NS15 compositions. Therefore, the silicon atoms appear to be unusually mobile in the NS30 compositions. Higher sodium concentrations break up the silica network structures, which may be causing the additional atomic movement. Alternatively, it may be indicative of an additional energy dissipation mechanism in NS30 compared to lower sodium compositions, which is discussed later in the manuscript.

The varying amount of sodium and silicon movement indicates that perhaps the sodium movement should be considered in terms of their movement *relative* to the rest of the structure. Generally, silicon atoms are the least mobile in the sodium silicate glass structure due to their inclusion in silica tetrahedron. Therefore, they have been used as the benchmark for sodium movement. The result in Figure 4-5.c., indicates that when the movement of the silicon atoms are removed from the analysis, the movement of the sodium within the first 10 Å of the crack tip becomes linear with composition, with the most movement occur in the NS10 structure (0.43 ± 0.25 Å) and the least in the NS30 structure (0.14 ± 0.05 Å). Therefore, while the NS20 and NS25 compositions exhibit more deviation from the linear trend for the *total* displacement within the first 10 Å of the crack tip, within this region the more sodium atoms are present, the less *relative* sodium movement occurs.

Yet, between 10-20 Å from the crack tip the trend shows more significant sodium movement in the NS15 and NS20 compositions. Perhaps even more interestingly, is that for the NS10 composition the radial sodium movement relative to the silicon atoms is *negative*. In our analysis, this would indicate that the sodium atoms are less mobile, or that the silicon atoms are moving faster and farther from the crack tip than the sodium atoms during loading. This observation is related to the higher mobility of sodium atoms for NS10 compositions within the first 10 Å of the crack tip. If the sodium atoms are experiencing a driving force towards the crack tip, this would cause them to be displaced contrary to the silicon atoms that are generally moving away from the crack tip due to the

far-field loading. Sodium movement towards surfaces based on concentration gradients is well documented on flat surfaces,¹¹⁴ and their movement towards the fracture surfaces here would be consistent with this analysis, though in a different geometry. Additionally, reports by San et al. and Cormack et al. identified multiple aspects of sodium movement, with fast sodium diffusion through undercoordinated tetrahedron.^{100, 115} While a detailed analysis of the mechanisms that cause the sodium movement in the quasi-statically loaded system is outside the scope of this investigation, it is clear that the unique structure near the crack tip has the ability to alter sodium movement and possibly create a stress-driven mechanism. The increased sodium atom mobility may provide some limited energy dissipation mechanisms in these brittle systems.

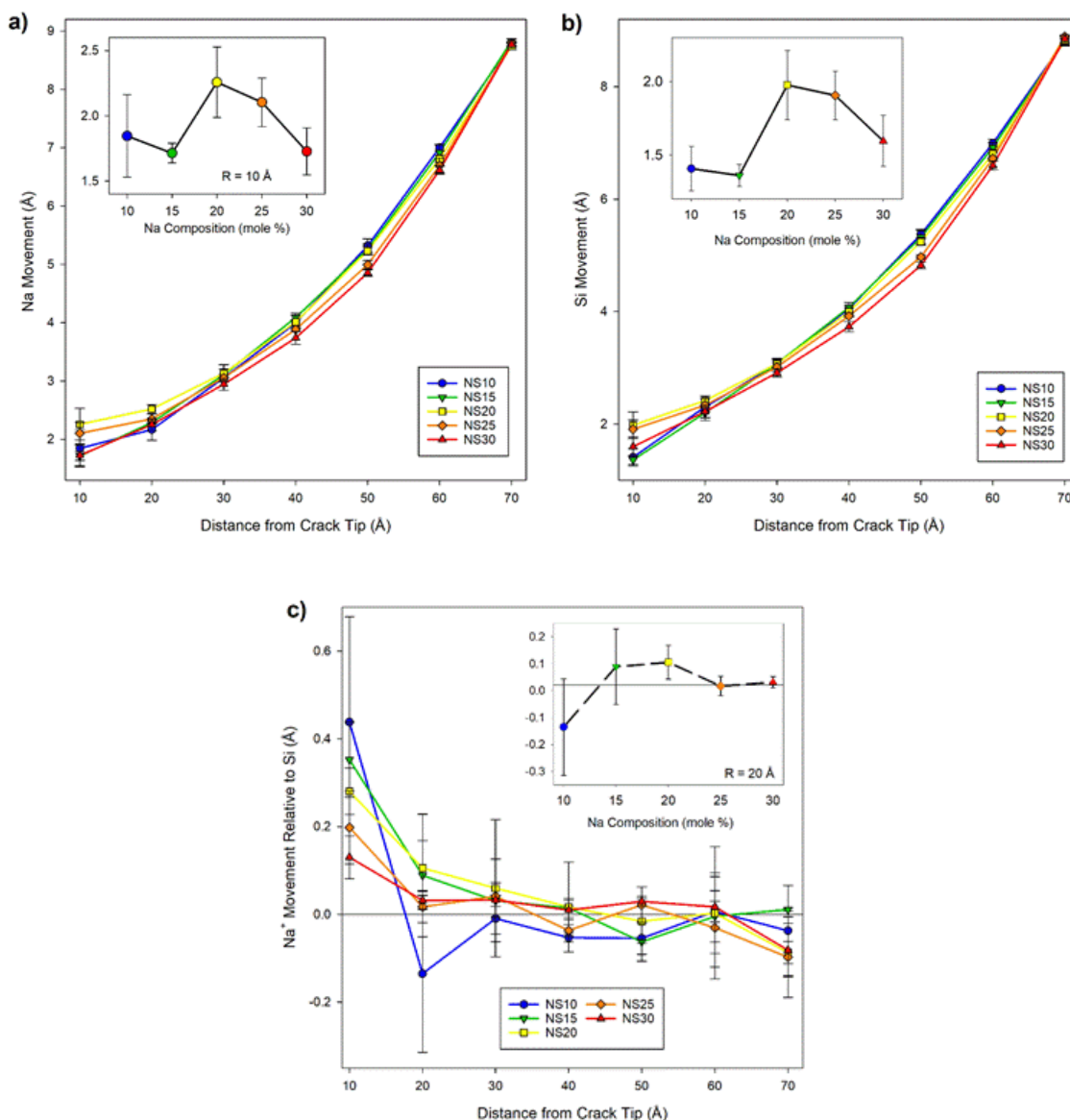


Figure 4-5: Average (a) sodium movement, (b) silicon movement, and (c) sodium movement relative to silicon as a function of distance from the crack tip. All data is the radially averaged movement (based on atom type) between 0.2 and 1.2 MPa√m of quasi-static loading.

While the Na is responsible for the bulk of the rearrangement of the glass structure, some *limited* changes in the silica network are also occurring. To quantify this effect, we have evaluated changes in the silica network structure, including the changes in the Q_n distribution, the concentrations of defect structures, and the intermediate range ring structure. Overall, there are limited changes in the network, especially compared to the effect of compositional differences. The change in Q_n distribution at $K_I = 0.2 \text{ MPa}\sqrt{\text{m}}$ and at $1.2 \text{ MPa}\sqrt{\text{m}}$ is included in Table 4-4, with changes in the Q_n distribution between 0.1% to 0.3% following loading. Similarly, the ring structures were virtually unchanged during loading.

Table 4-4: Q_n concentration at initial $0.2 \text{ MPa}\sqrt{\text{m}}$ loading and at $1.2 \text{ MPa}\sqrt{\text{m}}$ as a function of sodium concentration in sodium silicate glasses

	Loading ($\text{MPa}\sqrt{\text{m}}$)	Q_1	Q_2	Q_3	Q_4	Q_5	Connectivity
NS10	0.2	0.08 ± 0.02	1.57 ± 0.08	20.20 ± 0.06	77.92 ± 0.17	0.23 ± 0.06	3.766
	1.2	0.08 ± 0.02	1.58 ± 0.10	20.22 ± 0.07	77.89 ± 0.16	0.23 ± 0.06	3.766
NS15	0.2	0.13 ± 0.01	3.58 ± 0.06	28.35 ± 0.10	67.78 ± 0.06	0.16 ± 0.03	3.643
	1.2	0.17 ± 0.03	3.60 ± 0.08	28.35 ± 0.24	67.72 ± 0.35	0.17 ± 0.03	3.641
NS20	0.2	0.58 ± 0.01	6.28 ± 0.06	37.16 ± 0.17	55.83 ± 0.15	0.15 ± 0.07	3.473
	1.2	0.58 ± 0.01	6.27 ± 0.06	37.18 ± 0.14	55.81 ± 0.16	0.16 ± 0.07	3.473
NS25	0.2	1.12 ± 0.02	10.81 ± 0.10	41.32 ± 0.08	46.66 ± 0.17	0.09 ± 0.04	3.338
	1.2	1.12 ± 0.01	10.96 ± 0.28	41.29 ± 0.12	46.54 ± 0.33	0.09 ± 0.04	3.335
NS30	0.2	2.20 ± 0.01	16.87 ± 0.09	44.99 ± 0.05	35.88 ± 0.03	0.06 ± 0.02	3.147
	1.2	2.20 ± 0.01	16.87 ± 0.09	45.01 ± 0.05	35.86 ± 0.03	0.06 ± 0.02	3.147

The changes that are occurring in the system do highlight differences in the response of the sodium silicate glass structures to the quasi-static loading. Figure 4-6 includes the total change in defects in the system between the initial state ($0.2 \text{ MPa}\sqrt{\text{m}}$), an intermediate state ($0.5 \text{ MPa}\sqrt{\text{m}}$), and a final state ($1.2 \text{ MPa}\sqrt{\text{m}}$). Both Q_n and coordination defects are included in the analysis. Q_n is the number of BO atoms associated with a single silicon atom, so that a Q_4 species would be silicon atom coordinated by four BOs. Other Q_n species (Q_1 , Q_2 , Q_3 , and Q_5) are all identified as defect species. Additionally, coordination structure defects such as NBO, TBO, Si^1 , Si^2 or Si^3 have been considered.

As seen in Figure 4-6.a. there are small but measurable changes in the defect concentration with composition. For NS10, NS15, and NS20 compositions, the change in defects is slightly negative, with the decrease in Q_n defects being balanced by the increase in coordination defects. This balance of Q_n and coordination defects would be expected with breakage of individual bonds during loading and the formation of surfaces. Interestingly, the NS20 compositions exhibit the least change in defect concentration overall, with the lowest change in coordination and Q_n defects following $0.5 \text{ MPa}\sqrt{\text{m}}$ of loading, despite the elevated sodium mobility. For higher sodium concentration compositions (NS25, NS30) both the number of Q_n and coordination defects increases during loading, causing the largest amount of defect formation for the NS30 composition. The global increase in defects indicates that there are mechanisms that are introducing defects into the system that are separate from simple bond breakage and formation. The formation of coordination defects *not* at the expense of Q_n defects also indicates the existence of Si-O bond breakage events not associated with the formation of

surfaces. For instance, in Figure 4-6.b. the NS30 composition is forming a higher total number of defects than the NS20 compositions, despite forming half as much surface area after 1.2 Mpa $\sqrt{m}$ of loading. Therefore, the higher dissipation energy noted in the NS30 sodium silicate glass composition can be attributed to the formation of Q_n and coordination defects in the process zone that are not associated with the change in the fracture surface area.

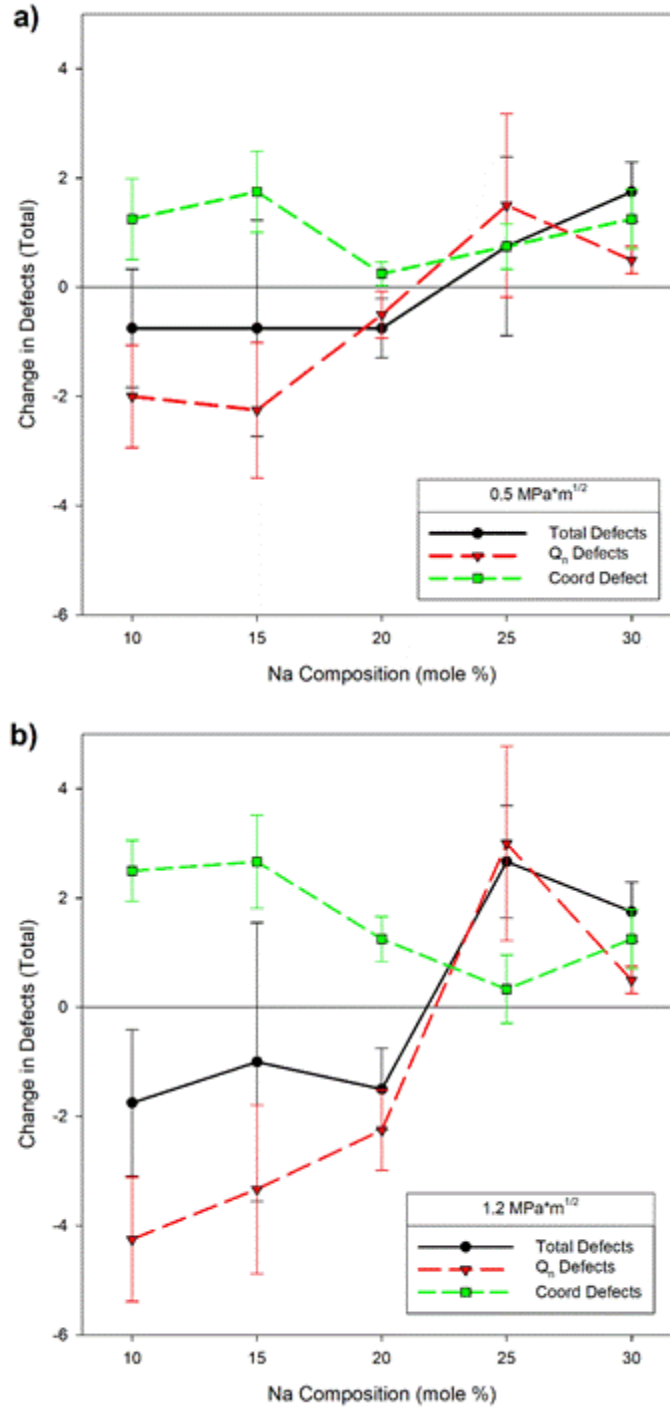


Figure 4-6: Change in total, Q_n , and coordination defects after from initial loading (0.2 Mpa $\sqrt{m}$) to either (a) 0.5 Mpa $\sqrt{m}$ or (b) 1.2 Mpa $\sqrt{m}$ as a function of sodium concentration.

4.5. Conclusion/Summary

Reactive classical MD simulations of sodium silicate glasses under mode I quasi-static loading were used to evaluate molecular scale fracture mechanisms. The calculated mechanical properties were verified to be consistent with experimental reported values. Over the range of 10-30 mole % Na_2O , the most crack propagation occurred in NS20 systems (20 mole % Na_2O). To quantify the amount of energy in the system that is lost to inelastic mechanisms (e.g., defect formation), rather than the formation of high energy surfaces, G_{DISS} was calculated based on the change in surface area and internal energy. The system with the highest crack propagation (NS20) also exhibited some of the lowest energy dissipation, indicating that the system has more brittle character than the other sodium silicate glass compositions. Analysis of the sodium movement within the 65 Å process zone around the crack tip identified that the NS20 compositions exhibited the most sodium and silicon movement within the first 10 Å of the crack tip. In comparison, the NS30 structure with the least amount of fracture propagation had limited sodium movement, but higher amounts of silicon atom movement within the first 10 Å of the crack tip, indicating that the silica network structure is being influenced by the high stress as the crack tip.

Further evaluation of coordination and Q_n defect structures identified that this higher silicon movement in the NS30 structures resulted in increases in both types of defects within the process zone and a net increase in defects over the course of the quasi-static loading. In comparison, for the NS20 and lower sodium compositions the change in defects was balanced between Q_n and coordination defects indicating of the formation of surfaces, but not additional defect formation in the process zone. Therefore, in the higher sodium compositions, the energy dissipation appears to be primarily through defect formation, while for lower sodium composition it is through the formation of surface area. Overall, the response of both the sodium network modifiers and the silica network structure in the highly stressed process zone surrounding the crack tip impact the ability of a fracture to propagate.

5. FREELY JOINTED CHAIN MODELS WITH EXTENSIBLE LINKS

5.1. Overview

Analytical relations for the mechanical response of single polymer chains are valuable for modeling purposes, on both the molecular and the continuum scale. These relations can be obtained using statistical thermodynamics and an idealized single-chain model, such as the freely jointed chain model. To include bond stretching, the rigid links in the freely jointed chain model can be made extensible, but this almost always renders the model analytically intractable. Here, an asymptotically correct statistical thermodynamic theory is used to develop analytic approximations for the single-chain mechanical response of this model. The accuracy of these approximations is demonstrated using several link potential energy functions. This approach can be applied to other single-chain models, and to molecular stretching in general. This chapter is adapted from: Buche, Michael R., Meredith N. Silberstein, and Scott J. Grutzik. "Freely jointed chain models with extensible links." *Physical Review E* 106.2 (2022): 024502. (doi.org/10.1103/PhysRevE.106.024502)

5.2. Introduction

The mechanical response of a single polymer chain can be obtained by measuring the end-to-end length as a function of an applied force. For small forces, this single-chain mechanical response is primarily due to the reduction in entropy as the chain is extended.¹¹⁶ Idealized single-chain models, such as the freely jointed chain model, allow quantification of these physics. The FJC model consists of a series of rigid links connected by penalty-free hinges.¹¹⁷ Using statistical thermodynamics¹¹⁸, the single-chain mechanical response can be obtained in closed-form in terms of the Langevin function.¹¹⁹ For large forces, bonds begin to stretch in the real chain, so that the rigid links of the FJC model should be extensible using a potential energy function.¹²⁰ Though the same thermodynamic principles apply¹²¹, the necessary configuration integrals almost always become analytically intractable. Currently, the only known exactly solvable model is the particular case of harmonic link potentials.¹²²⁻¹²³ This is challenging since exact relations enable more efficient modeling and a deeper fundamental understanding. Analytic approximations are a good alternative, since they are efficient and often quite accurate. A variety of approaches that have been developed to approximate the single-chain mechanical response of freely jointed chains with extensible links. The simplest approach is to modify the Langevin function of the FJC single-chain mechanical response to yield the correct high-force behavior for a given link stiffness.¹²⁴ Additional terms can be included for improved approximation of the harmonic potentials,^{122, 125} enabling better accuracy at lower link stiffnesses and more robust modeling.^{121, 126} This simple approach can be generalized for anharmonic link potentials to capture the mechanical response up until the chain breaks, which is used for large-deformation polymer network constitutive models.^{120, 127} An alternative approach has been developed by Mao et al.¹²⁸, where a constructed free-energy function is minimized with respect to link length in order to obtain an effective link length, and subsequently the single-chain mechanical response. This approach has been utilized quite frequently in polymer network constitutive models, using both harmonic¹²⁹ and anharmonic¹³⁰ link potential energy functions, though it is heuristic to minimize thermodynamic free energies with respect to phase space degrees of freedom.¹²⁰ Despite this progress, a more complete approach of approximating the single-chain mechanical response of freely jointed chains with extensible links is still needed. Critically, there are no approaches that are accurate in a well-understood regime of model parameters. Further, any reliable approach would need to begin from and closely adhere to the principles of statistical thermodynamics. Here, such an approach is developed using an asymptotically correct statistical thermodynamic theory.¹³¹

5.3. Theory

The FJC model consists of N_b rigid links of length b and they are connected in series by penalty-free hinges.¹¹⁶ This single-chain model is generalized to the uFJC model by assigning some potential energy function (u) to each link and allowing the link length to fluctuate away from its rest length (b).¹²⁰ Here the isotensional ensemble is considered, where a fixed force (f) is applied to the chain, and the expected chain end-to-end length (ξ) was calculated using the partition function.¹²³ T was also fixed, or equivalently $\beta = 1/k_B T$ is fixed. Asymptotically correct relations, valid for steep link potentials¹³¹, are obtained for the isotensional partition function and are used to obtain the isotensional mechanical response. Steep potentials are characterized by large scale and stiffness compared with thermal energy, i.e., steep potentials are both deep and narrow. An asymptotic relation for low to intermediate forces was obtained first, then another for high forces, and finally the two are matched in a composite relation for all forces. A reduced form of this relation is provided, which becomes accurate in the limit of sufficiently steep link potentials. A full derivation of the modeling, including considerations for low-to-intermediate force asymptotics, high-force asymptotics, and matched asymptotics for all forces are included in Section II.a through Section II.c. in Ref¹³².

5.4. Results

The full asymptotic approach and the reduced asymptotic approach are demonstrated in approximating the single-chain mechanical response of the uFJC model. The harmonic link potential (the EFJC model) is considered first, followed by the log-squared potential, the Morse potential, and the Lennard-Jones potential. The asymptotic approaches are compared with an exact solution when available, and numerical quadrature otherwise. Calculations were completed using the Python package uFJC. Using harmonic link potentials with the uFJC model produces the EFJC model; the scaled nondimensional potential energy function in this case is

$$\phi(s) = \frac{1}{2}(s - 1)^2 \quad (5-1) \quad \text{Though the}$$

specifics can be different, the harmonic potential is the most common way of rendering the rigid links of the FJC model extensible^{121, 133}. The full asymptotic, reduced asymptotic, and exact approaches of obtaining the EFJC single-chain mechanical response $\gamma(\eta)$ are plotted in Figure 5-1 while varying the link stiffness κ . These results are given in terms of the scaled nondimensional force $\tau \equiv \eta/\epsilon$. The full asymptotic approach is negligibly different from the exact approach for all values of κ due to the full asymptotic approximation being exactly correct to within transcendentally small terms in the case of harmonic links. The reduced asymptotic approach tends to be inaccurate for moderate κ , but quickly becomes accurate for large κ . Above $\kappa = 100$, the difference between all three apparently vanishes, where the reduced asymptotic approach could be used in place of the exact approach for expediency since κ is often larger than 100 when modeling experiments.¹³⁴

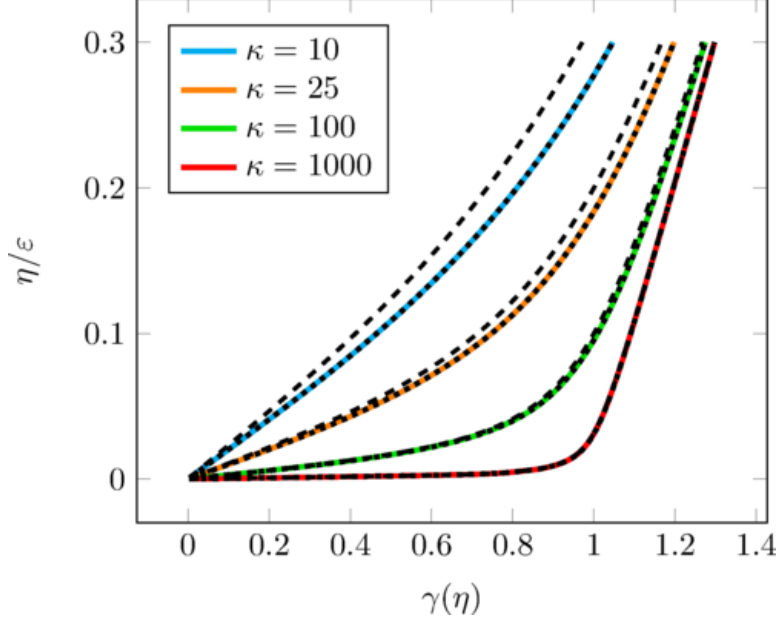


Figure 5-1: The nondimensional single-chain mechanical response $\gamma(\eta)$ for the EFJC model, using the full asymptotic (dotted), reduced asymptotic (dashed), and exact (solid) approaches, for varying nondimensional link stiffness $\kappa = \epsilon$.

When link stretches are large, the chosen link potential energy functions are anharmonic and escapable. Similarly, to using true strain in place of engineering strain in a continuum model, the harmonic potential can be replaced with the log-squared potential¹²⁸. The scaled nondimensional potential energy function in this case is:

$$\phi(s) = \frac{1}{2}[\ln(s)]^2 \quad (5-2)$$

The asymptotic approaches are compared with the quadrature results for varying κ in Figure 5-2, where η is scaled by $\eta_{\max} = \epsilon/e$.

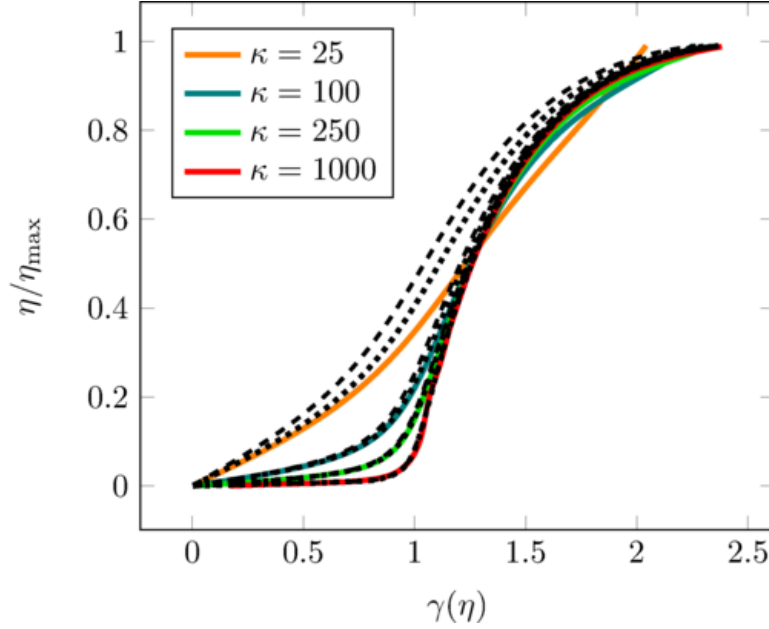


Figure 5-2: The nondimensional single-chain mechanical response $\gamma(\eta)$ for the log-squared-FJC model, using the full asymptotic (dotted), reduced asymptotic (dashed), and quadrature (solid) approaches, for varying $\kappa = \epsilon$.

While the full asymptotic approach does perform better (in matching the quadrature approach), neither asymptotic approach is accurate until κ reaches 100 and above. The Morse potential¹³⁵ is another common choice for the link potential energy function of the uFJC model^{120, 136-137}. The scaled nondimensional Morse potential energy function is:

$$\phi(s) = [1 - e^{-\alpha(s-1)}]^2 \quad (5-3)$$

where α is the Morse parameter, related to the nondimensional stiffness $\kappa = 2\alpha^2\epsilon$. The asymptotic approaches are compared with the quadrature results for varying κ in Figure 5-3, where η is scaled by $\eta_{\max} = \alpha\epsilon/2$. Figure 5-3 illustrates an important pathology of the quadrature approach that appears when dealing with escapable potentials, such as the Morse potential. For insufficiently steep link potentials, this constraint is nonphysical and results in artificial strain-stiffening in the anharmonic regime, rather than the expected strain-softening of an escapable potential. As the link potential becomes sufficiently steep, this pathology vanishes, and the expected behavior is obtained; all of this is seen clearly in Figure 5-3. In short, any approach for breakable links is only valid when the link potentials are sufficiently steep. Figure 5-3 shows that the full asymptotic approach matches the quadrature approach more closely than the reduced asymptotic method does, and that all three methods converge as κ becomes large. In addition to being more interpretable and computationally expedient, the asymptotic methods do not suffer from the artificial strain-stiffening pathology. It would then be best to utilize the asymptotic approaches developed here when stretching breakable molecules.

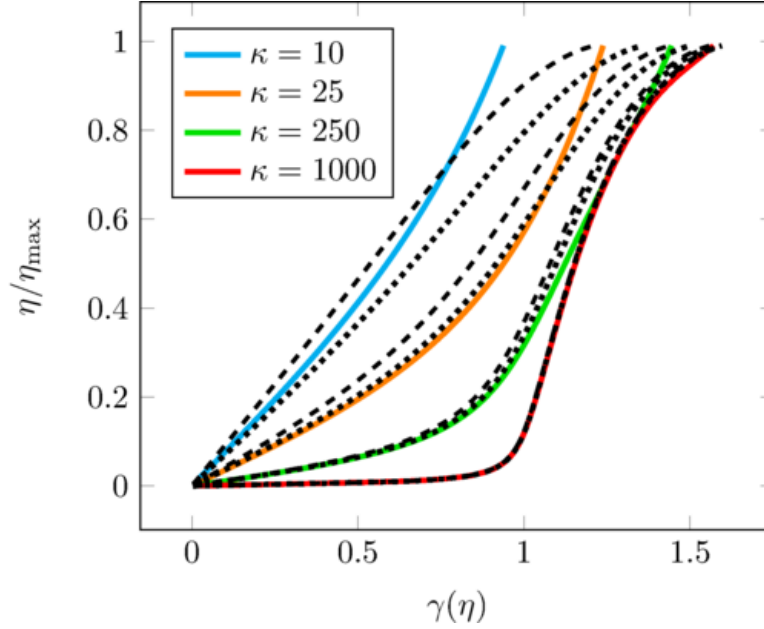


Figure 5-3: The nondimensional single-chain mechanical response $\gamma(\eta)$ for the Morse-FJC model ($\alpha = 1$), using the full asymptotic (dotted), reduced asymptotic (dashed), and quadrature (solid) approaches, for varying $\kappa = 2\alpha 2\epsilon$.

Finally, the Lennard-Jones potential¹³⁸ can also be used as the link potential energy function¹³⁹. The scaled nondimensional potential energy function in this case is:

$$\phi(s) = \frac{1}{s^{12}} - \frac{2}{s^6} \quad (5-4)$$

The asymptotic approaches are compared with the quadrature results for varying κ in Figure 5-4, where η is scaled by $\eta_{\max} = 12\epsilon[(7/13)^{7/6} - (7/13)^{13/6}]$. Each asymptotic approach converges for large κ , but the reduced asymptotic approach tends to match the quadrature approach more closely than the full asymptotic approach. The Lennard-Jones potential is escapable, so the strain-stiffening pathology of the quadrature approach is also observed in Figure 5-4. Since the nondimensional stiffness is nearly two orders of magnitude different from the nondimensional energy scale, κ must be large for ϵ to also be sufficiently large to consider the potential steep. This results in higher values of κ being required for the approaches to converge in Figure 5-4 compared to the previous cases. Note that the quadrature approach is not necessarily accurate for lower values of κ , so the reduced asymptotic approach matching more closely in Figure 5-4 could be misleading. To further analyze the steep potential requirement, one can consider an opposing case in which the energy scale is high but the stiffness is low, or even zero: the square-well potential.¹¹⁸ The asymptotic approach cannot be applied at all in this case, even though the results do approach that of the reference system (FJC) as the potential narrows.

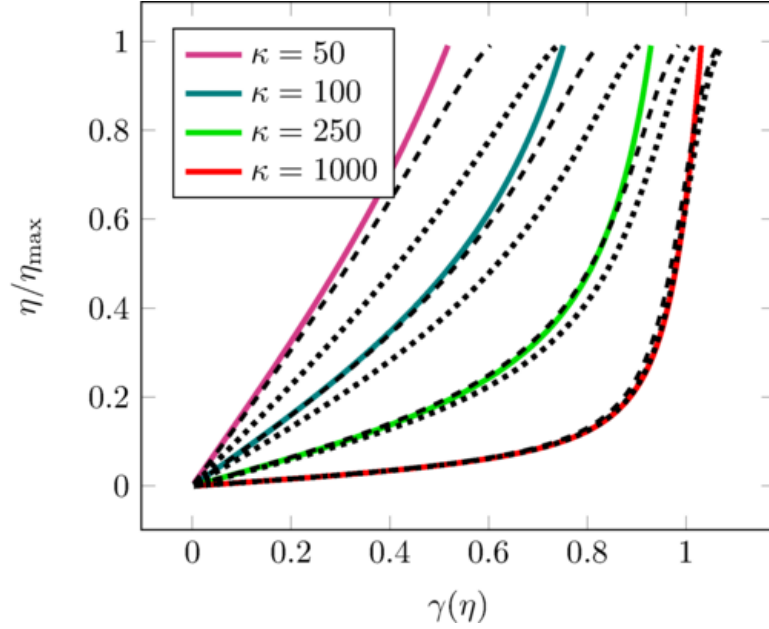


Figure 5-4: The nondimensional single-chain mechanical response $\gamma(\eta)$ for the Lennard-Jones-FJC model, using the full asymptotic (dotted), reduced asymptotic (dashed), and quadrature (solid) approaches, for varying $\kappa = 72\epsilon$

5.5. Conclusions

An asymptotically correct statistical thermodynamic theory has been applied to develop analytic approximations for the single-chain mechanical response of freely jointed chains with extensible links, i.e., the uFJC model. The full asymptotic relation contains both entropic and enthalpic contributions as well as the coupling between them; when this coupling is neglected, the reduced asymptotic relation is obtained. These asymptotic relations are valid as the link potential energy functions become steep, meaning both the potential energy scale as well as the stiffness become large compared with thermal energy. For escapable potentials, this steepness is also understood as the potential well being both deep and narrow. These asymptotic approaches were verified by comparing with the exact, analytic approach in the case of harmonic link potentials, using both parametric study and mathematical analysis. Parametric studies were performed for the log-squared, Morse, and Lennard-Jones potentials, where exact results were unavailable, and a quadrature approach was used. In each case, the asymptotic approaches became increasingly accurate as the potentials became steep. It was observed that the quadrature method suffers from an artificial strain-stiffening pathology for escapable potentials before the steep limit is met, which encourages use of the more robust asymptotic approaches. The success of this asymptotic approach as demonstrated here, using the freely jointed chain model as a reference system, indicates probable success for general molecular stretching models. While even reference systems are often analytically intractable, this asymptotic approach can still be applied on an approximation for the reference system to obtain one for the full system.

6. SLOW CRACK GROWTH IN ALKALI SILICATE GLASSES

6.1. Overview

Mechanical testing was performed on Schott-8061 glass and a series of binary sodium silicate glasses with the nominal molar composition $x\text{Na}_2\text{O} \cdot (100-x)\text{SiO}_2$, where $x = 15, 25$, and 35 . The DCB method was used to measure the sub-critical crack velocity in the three regions described by Weiderhorn¹⁴⁰: Region I, where crack velocity is controlled by the glass-water reaction rate; Region II, where crack velocity is limited by the water transport rate; and Region III where crack velocity depends on the influence that water has on the energy associated with the creation of fracture surface. Crack arrest was noted in DCB samples from the $35\text{Na}_2\text{O} \cdot 65\text{SiO}_2$ glass tested in room temperature air at 70% RH and is explained by capillary action that pulled water directly to the crack tip. When this glass was tested in air with 3% RH, stable crack extension in Region I was observed and could be measured. Two-point bend measurements, performed on 100-micron diameter fibers drawn from each glass melt and tested in both room temperature deionized water and air at 70% RH recorded failure strains that were sensitive to the testing conditions and reproducible to better than 1% relative. n_{TPB} were calculated from the two-point bend data were used to empirically calculate Region I crack velocity with power-law. Empirical and measured data for Schott-8061 agreed between two-point bend, four-point-bend, and DCB. Mismatch in Region I crack velocity slopes for the sodium silicate series is likely due to mixed mechanisms taking effect when testing in high humidity environments. In general, greater values for the n_{TPB} for the binary sodium silicate glasses were calculated from two-point bending data collected in air at 70% RH and were more in line with values determined from the DCB tests.

6.2. Methods

A series of sodium silicate glasses were synthesized with the nominal molar composition $x\text{Na}_2\text{O} \cdot (100-x)\text{SiO}_2$, where $x = 15, 25$, and 35 . Raw materials Na_2CO_3 (Fisher Science, $\geq 99.5\%$ purity) and SiO_2 (Alfa Aesar, 99.5% purity) were batched, mixed and transferred to a platinum-rhodium crucible and melted in an air furnace using the conditions summarized in Table 6-1. The melts were stirred with a platinum rod every hour for 3 hours, then left undisturbed for the final hour to allow any remaining bubbles to fine. Melts were poured into a 64x100 mm preheated graphite mold and annealed at $T_{\text{anneal},1}$ for 2 hours, annealed at $T_{\text{anneal},2}$ for 2 hours, then cooled to room temperature. Commercially available Schott-8061 glass was tested along with the sodium silicates as comparison of a complex glass.

Table 6-1. T_{melt} , t_{melt} , T_{anneal} , and t_{anneal} for glasses prepared in the laboratory

Glass Composition	T_{melt} (°C)	t_{melt} (hr)	$T_{\text{anneal},1}$ (°C)	$t_{\text{anneal},1}$ (hr)	$T_{\text{anneal},2}$ (°C)	$t_{\text{anneal},2}$ (hr)
$15\text{Na}_2\text{O} \cdot 85\text{SiO}_2$	1650	4	485	2	435	2
$25\text{Na}_2\text{O} \cdot 75\text{SiO}_2$	1500	4	470	2	420	2
$35\text{Na}_2\text{O} \cdot 65\text{SiO}_2$	1250	4	450	2	400	2
Schott 8061	1500	4	460	2	410	2

Annealed glasses were machined (Bomas Machine Specialties, Inc) into one of five different types of samples for mechanical testing; sample dimensions are given in Table 6-2. The DCB samples were

also machined with a 1.25 mm width central square groove down the length of each sample at a depth of 0.65 mm. Each DCDC sample had a 1.0 mm diameter hole drilled through its center.

Table 6-2: Geometries of samples prepared for mechanical testing

Sample	Dimensions
Bi-beams	6.35 mm x 25 mm x 75mm
ASTM C1421 Bend Bars	3 mm x 4 mm x 50 mm
Constant Moment DCB	1.5 mm x 12.7 mm x 50.8 mm
Drilled Compression Double Cantilever	4 mm x 4 mm x 40 mm
DMA specimen	3 mm x 4 mm x 50 mm
Fibers	12.5 cm long, 100 mm diameter
TMA specimen	10 mm x 10 mm x 25 mm

Glass fibers were drawn from the surfaces of the Na-silicate and S-8061 glass melts using a process described elsewhere.¹¹⁰ Briefly, bubble-free melts were heated in a platinum crucible to the fiber-pulling temperature (melt viscosity about 10^4 Pa-s), and a fiber was drawn from the melt surface and attached to a rotating cage positioned above the melt. The cage then pulled continuous fibers about 100 μ m in diameter. The rotating cage used to draw the fibers had contact points approximately 15 cm apart. The fibers were cut to 12.5 cm in length between these contact points leaving pristine fibers that have not contacted any surface during the process. These fibers were used in the two-point bending experiments described below.

6.2.1. Subcritical Crack Growth

Subcritical crack growth velocities were measured using a constant moment DCB setup, similar to that described by Freiman (Figure 6-1).¹⁴¹ A two-part epoxy (Devcon) was used to attach the metal arms to the glass sample. The specimen was then notched using a 0.5 mm wide slow speed diamond saw to introduce an initial flaw for crack propagation. Notched samples were attached to the bending moment assembly in the plexiglass environmental chamber. Standard calibration weights were added until a crack began to propagate from the notch. The weights are then used to control mode I stress intensity factor, K_I , on the crack tip. K_I can be calculated from the following equations:

$$\mathcal{G} = \frac{M^2}{EIt} \quad (6-1)$$

$$K_I = \sqrt{\mathcal{G}E} \quad (6-2)$$

where $\mathcal{G}$ is the strain energy release rate, M is the bending moment (defined by the applied force times the distance between the applied weight and fulcrum of the attached arms), I is the moment of inertia, and t is the groove thickness. The dimensions of the groove were used to define I by:

$$I = \frac{bh^3 - aw^3}{3} - \frac{(bh^2 - aw^2)^2}{4(bh - aw)} \quad (6-3)$$

where, b is the sample thickness, h is the half the sample width, a is the depth of groove, and w is half the groove width.¹⁴² The cracks were imaged using an optical system that included an objective lens (20x) on a Point Grey camera (Richmond, BC, Canada) that collected images at up to 26 frames per second. ImageJ (version 1.41, U.S. National Institute of Health) was used to measure the crack length from videos recoded during testing.¹⁴³ Crack velocity was calculated from crack length and time between individual frames.

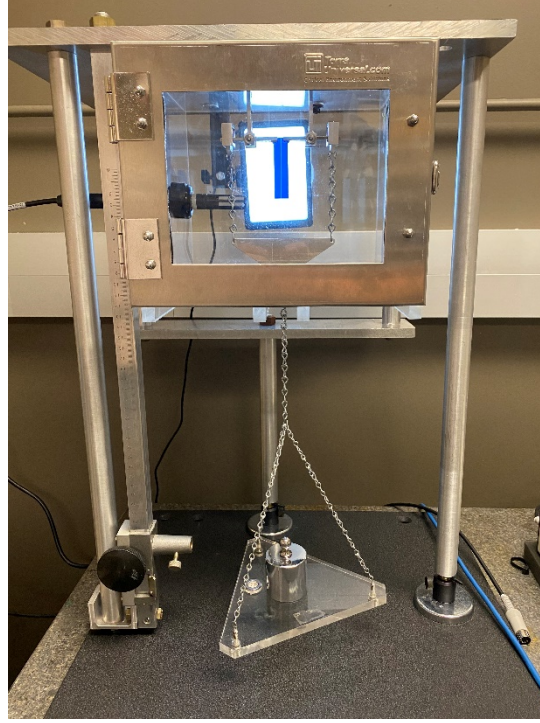


Figure 6-1: Constant moment double cantilever beam setup used to directly measure crack velocity

6.2.2. Two-Point Bend Testing

Fiber failure strains were measured using a two-point bending system (TNL Tool and Technology, LLC, Parnell IA), in room temperature DI water, liquid nitrogen (77K), or in air at different fixed relative humidity. TPB tests were conducted at constant faceplate velocities (V_{fp}), ranging from 5 to 4000 $\mu\text{m/s}$. Failure strain (ϵ_f) was calculated from the faceplate gap at failure (D) and the fiber diameter (d).¹⁴⁴

$$\epsilon_f = \frac{1.198d}{(D-d)} \quad (6-4)$$

A minimum of 20 fibers were tested for each testing conditions and the two-point bending failure strain results are presented using the Weibull formalism:

$$P_f = 1 - \exp\left[\left(\frac{\epsilon_f}{\epsilon_{f,0}}\right)^m\right] \quad (6-5)$$

where P_f is the probability of failure and m is the Weibull modulus and $\epsilon_{f,0}$ is a scaling parameter, a. The Weibull plots were used to ensure that only a single source of flaws were tested and secondary handling flaws. The n_{TPB} was calculated from the faceplate velocity dependence of the failure strains measured in DI water and air.¹⁴⁵

$$n_{TPB} = 1 + 1/\left(\frac{d \log(\epsilon_f)}{d \log(v_{fp})}\right) \quad (6-6)$$

n_{TPB} measured by two-point bending are compared below to values calculated from the crack velocity measurements (n_{KV}) using an empirical power-law relation described in ASTM C1368, according to:

$$v = \frac{da}{dt} = AK_I^{n_{KV}} = A^* \left(\frac{K_I}{K_{IC}}\right)^{n_{KV}} \quad (6-7)$$

where A^* is the slow crack growth parameter, K_I is the mode I stress intensity factor, and K_{IC} is fracture toughness under mode I loading.¹⁴¹

6.2.3. Thermal Analyses

Glass transition temperatures were determined by DSC (TA Instruments, DSC Q2000). Samples were heated in nitrogen at a rate of 10°C/min. Glasses were ground down using a mortar and pestle then passed through sieve stack. Powder particle size used for analysis was between 100 and 120 μm .

TMA (Netzsch TMA 402 F1) was used to characterize the CTE and the T_g of each glass. Glass samples were cut into rectangular prisms (Table 6-2), ensuring that the long axis faces were parallel to one another. The samples were placed vertically between two alumina spacers then beneath the TMA piston rod. The sodium silicate glasses were heated in nitrogen at a ramp rate of 3°C/min, and the Schott 8061 sample was heated in nitrogen at 5°C/min to 600°C. Some tests ended at lower temperatures due to the software's safety function that ends tests when the glass contracts by more than 50% after softening. CTE values are reported between 100 and 350°C.

DMA (Netzsch DMA GABO Explexor) was performed on the Na-silicate glass samples (Table 6-2) using a three-point configuration (Figure 6-2). Tests were run from 25-400°C, with a ramp rate of 1°C/min, 30N static load, 10N dynamic load and a frequency of 2 Hz.

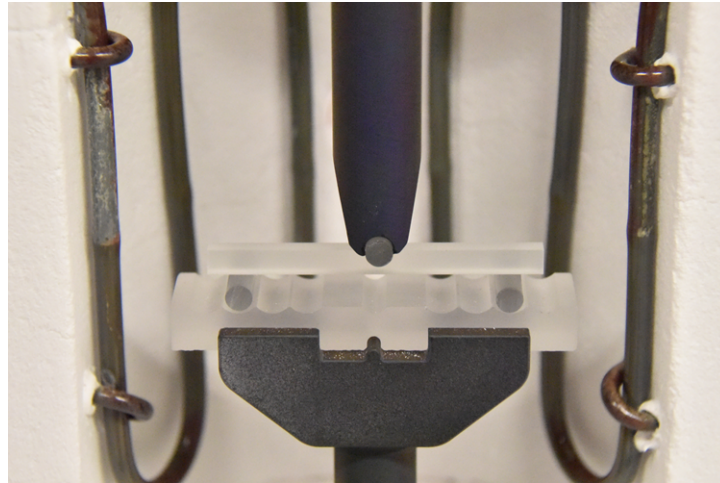


Figure 6-2: DMA setup with 15Na₂O·85SiO₂ glass composition in 3-point bend

6.2.4. Spectroscopic Studies

Raman spectra were collected with a LABRAM HR S3000 spectrometer (Jobin Yvon/Horiba group, Tokyo Japan). The excitation laser used was a diode-pumped solid-state laser system produced by Laser Quantum that was operated at 532nm. To correct for device fluctuations, a standard Argon

lamp emission line (696.54nm) was monitored. 5x5 μ m spot size areas were analyzed utilizing the LabRAM Duoscan™ features that generate a rastered laser spot. Data collected were then analyzed using LabSpec 6 (Jobin Yvon/Horiba Group) to fit peaks and output peak positions.

6.2.5. Fracture Toughness

The fracture toughness of the sodium silicate glasses was determined using the SEPB method, described in ASTM C-1421. The machined SEPB samples (Table 6-2) were cleaned with DI water, rinsed with ethanol, and then re-annealed to remove any residual stress resulting from machining. A Zwick Test Control II automated indenter was used to create nine Vickers indents laterally along the center of the bottom surface of each sample. Indents were produced with 9.81N load, held for 15s, and evenly spaced 0.3 mm apart from one another. Indented samples were then loaded in a bridge cracking assembly with 6 mm gap, shown in Figure 6-3. A load was applied to the assembly (Instron 5565) at a rate of 0.05 mm/min. The load was removed when a crack popped in, as detected by an acoustic sensor. Samples were then removed from the bridge precrack assembly and gently placed into a common 4-point flexure loading fixture, shown in Figure 6-4. Here the load at a rate of 0.05 mm/min until failure. Both precrack and failure loading were conducted in dry N₂ atmosphere with relative humidity below 0.8% and a temperature of 25°C. Fractographic analyses were conducted on the fracture surfaces of each sample to measure the precrack length needed to calculate fracture toughness. Fractography was conducted on a Keyence VHX-7000, utilizing a VH-Z20R lens with x20-x200 magnification. Eight samples of each composition were tested and then averaged to determine the fracture toughness for the composition.

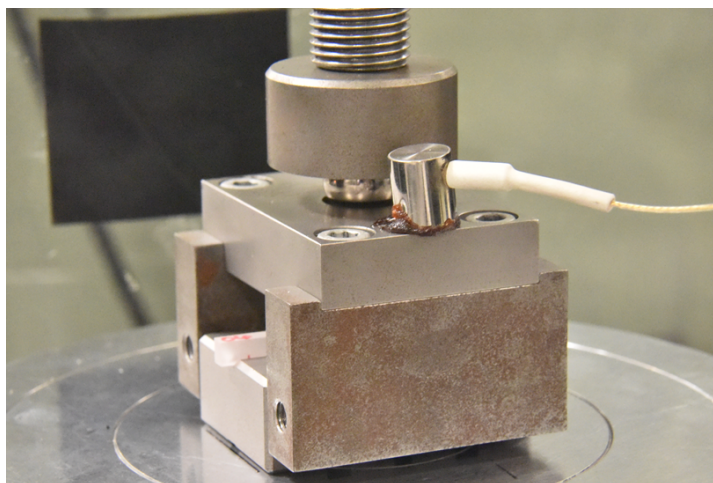


Figure 6-3: Bridge pre-crack assembly with 6 mm center gap

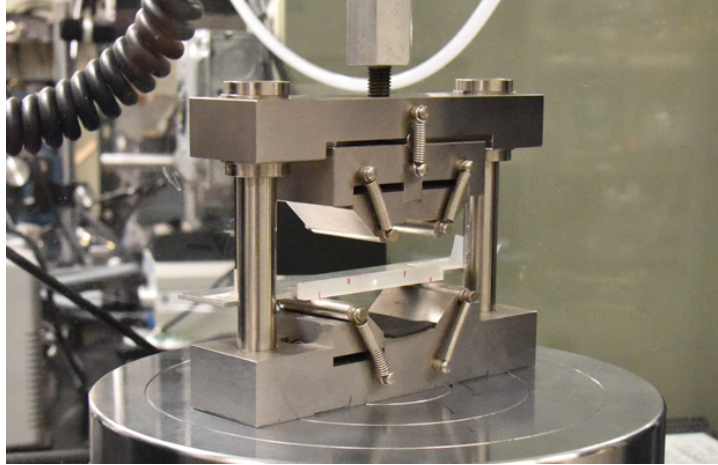


Figure 6-4: Common 4-point flexure loading assembly

6.2.6. Time of Flight - Secondary Mass Spectroscopy (ToF-SIMS)

ToF-SIMSs (from Ion-TOF) was used to characterize the composition along the fracture surface of the DCB samples. A depth profile was used to quantitatively determine the sodium concentration across areas of the DCB sample, which correlated to specific crack velocities. Both sides of the DCB sample were fitted between two microscope slides to increase scan area then leveled to have all surfaces at the same height. Sample configuration can be seen in Figure 6-5.

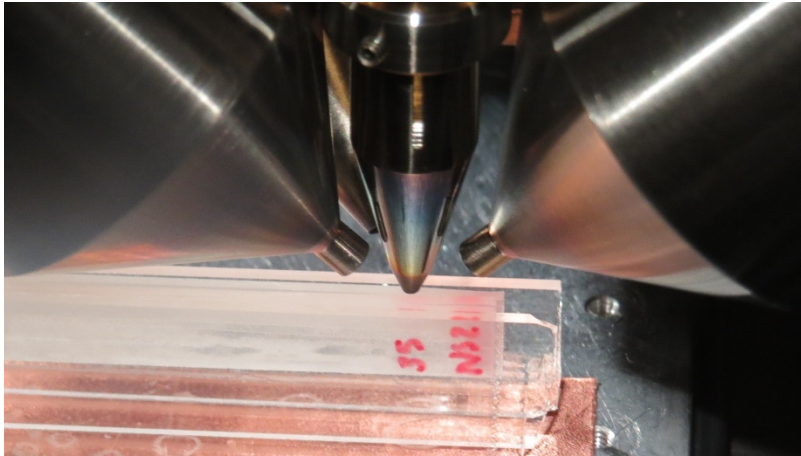


Figure 6-5: ToF-SIMS sample configuration with $35\text{Na}_2\text{O} \cdot 65\text{SiO}_2$ DCB sample

6.2.7. Resonant Ultrasound Spectroscopy (RUS)

RUS (Mangaflux RUSpec) was used to measure the elastic constants of the glass specimens. The parallel piped cuboid specimens were run with a frequency sweep (20 Hz – 200 kHz) and the measure peaks were compared to the resonant nodes calculated from the RUSpec software. The process was iterated until $<0.5\%$ error between the measured and calculated nodes. The elastic modulus was used to calculate K_I for the constant moment DCB testing.

6.3. Results

6.3.1. Thermal Analysis

Table 6-3 summarizes the data collected from TMA (left) and DSC data (right) for the sodium silicate glasses. With increasing soda contents, there is a decrease in T_g and an increase in CTE.

Table 6-3: Measured CTE and T_g values for sodium silicate glasses

Glass	TMA CTE ($^{\circ}\text{C}^{-1}$)	TMA T_g ($^{\circ}\text{C}$)	DSC T_g ($^{\circ}\text{C}$)
15Na ₂ O•85SiO ₂	7.88x10 ⁻⁶	478	488
25Na ₂ O•75SiO ₂	12.4x10 ⁻⁶	470	473
35Na ₂ O•65SiO ₂	15.3x10 ⁻⁶	448	452
Schott-8061	10.3x10 ⁻⁶	NA	NA

6.3.2. Fracture Toughness

Fracture toughness results using the SEPB method are shown in Table 6-4. Schott-8061 fracture toughness values reported in Table 6-4 are measured by Salem,¹⁴⁶ which show similar value and range of uncertainty to the sodium silicate series. All the sodium silicate series had comparable fracture toughness values within error.

Table 6-4: Fracture toughness values determined using SEPB method

Glass	Fracture Toughness (MPa•m ^{1/2})
15Na ₂ O•85SiO ₂	0.715±0.06
25Na ₂ O•75SiO ₂	0.685±0.05
35Na ₂ O•65SiO ₂	0.707±0.06
Schott-8061	0.720±0.02

6.3.3. Elastic Modulus

The elastic moduli values for the glasses are shown in Table 6-5. Both the values calculated from RUS and the room temperature DMA values are reported. The 35 mol% sodium silicate specimens did not produce a repeatable RUS signal for unknown reasons and is not reported. The good comparison between the RUS and DMA specimens gives confidence in the DMA results for the 35 mol% sodium silicate specimens.

Table 6-5: Elastic Moduli values from RUS and DMA

Glass	RUS (GPa)	DMA (GPa)
15Na ₂ O•85SiO ₂	62.5	60.9
25Na ₂ O•75SiO ₂	63.0	63.5
35Na ₂ O•65SiO ₂	N/A	59.1
Schott-8061	68.2	72.3

6.3.4. Crack Velocity Measurements

Crack velocities as a function of K_I , acquired from DCB testing, are shown in Figure 6-6. All samples were tested in relative humidities between 67-73%, except for the 35 mol% sodium composition which was tested in 3% relative humidity. Data set depicted below is a combination of multiple different samples for each of the glasses, where K_I is calculated according to each sample's dimensions. The magnitude of the crack velocity at a given K_I cannot be directly compared between glasses as the relative humidity has a large impact on the crack velocity. However, the slope of these lines can be used to calculate n_{TPB} and compared to the two-point bend method and will be discussed in the discussion section.

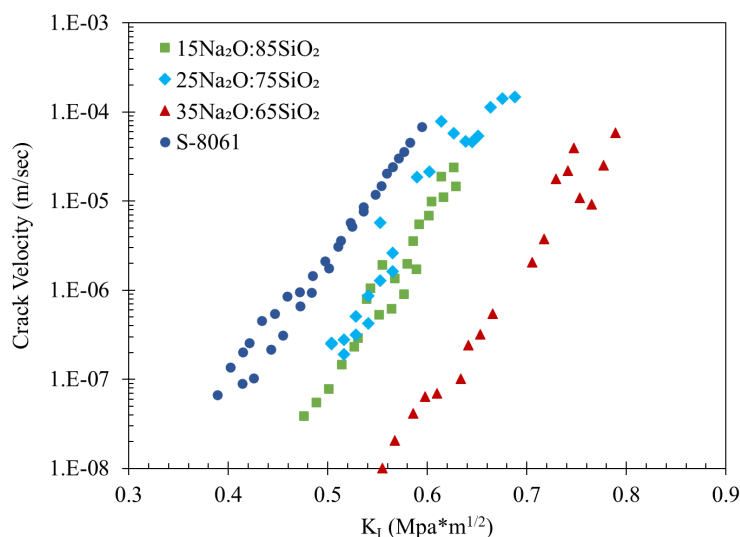


Figure 6-6: Crack velocity as a function of K_I for the various alkali silicate glasses

6.3.5. Two-Point Bend Failure Strain Measurements and Dynamic Fatigue

Figure 6-7 shows the TPB failure strain distributions, plotted using the Weibull formalism, for fibers drawn from each glass melt and tested at various faceplate velocities (V_{fp}) in room temperature water, data shown in black indicates glass fibers tested in an environmental chamber with 70% relative humidity. There is a systematic decrease in failure strain with decreasing V_{fp} , consistent with fatigue effects influencing the failure conditions. Figure 6-8 compares both a slow faceplate velocity of 5 $\mu\text{m/s}$ and the fast 4000 $\mu\text{m/s}$ to analyze the dependence of failure strain on glass composition.

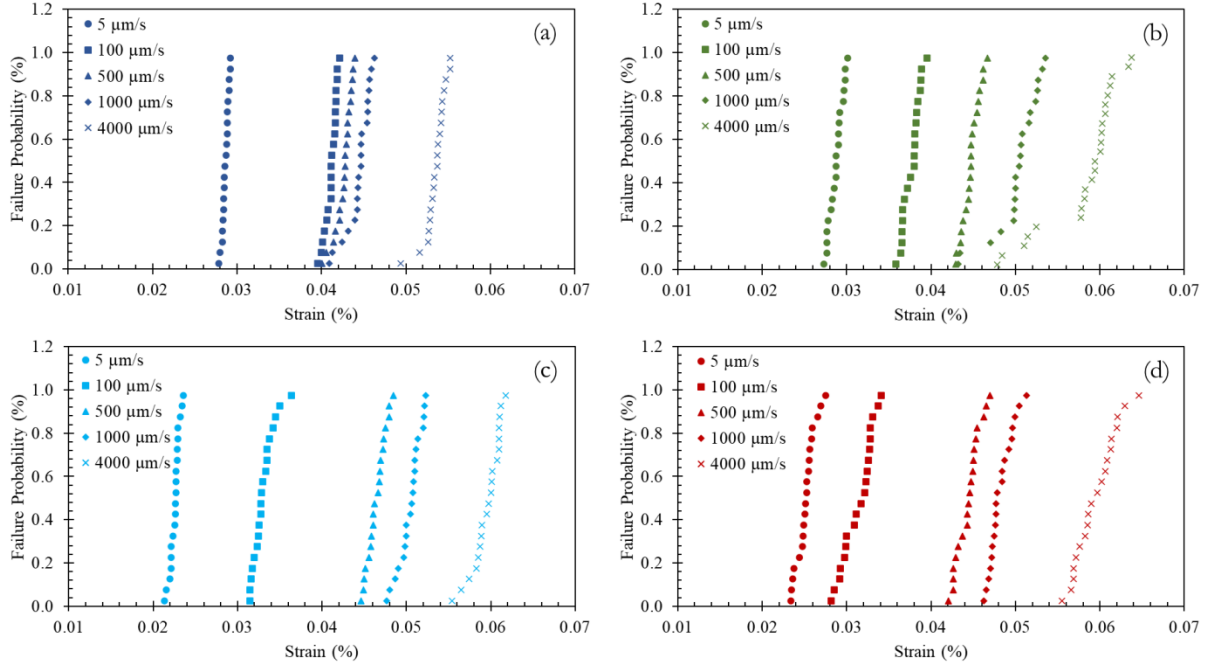


Figure 6-7: Failure probability as a function of strain for (a) Schott-8061, (b) $15\text{Na}_2\text{O}\cdot 85\text{SiO}_2$, (c) $15\text{Na}_2\text{O}\cdot 85\text{SiO}_2$, and (d) $15\text{Na}_2\text{O}\cdot 85\text{SiO}_2$ glass compositions

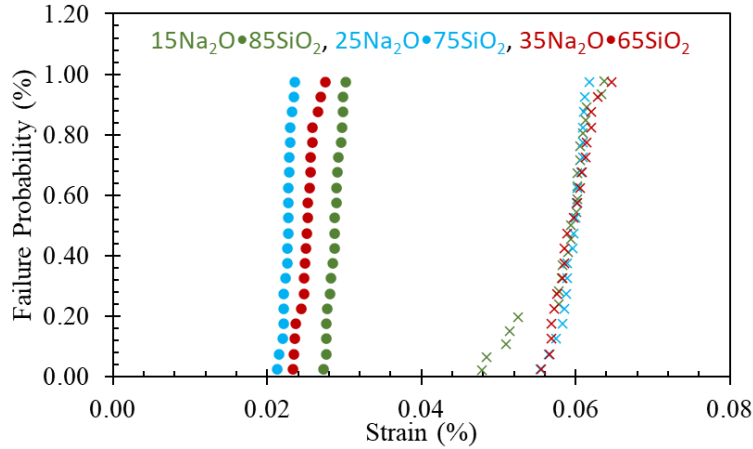


Figure 6-8: Dependence of failure strain on glass composition for 5 and 4000 $\mu\text{m/s}$ V_{fp}

n_{TPB} were calculated from the linear regression of the faceplate velocity-dependence of the average failure strain and using the slope of that regression fit with Equation 6-6. Figure 6-9 shows the linear regression fits to the failure strain data for all four glasses, and Table 6-6 summarizes the fitting parameters and the calculated values n_{TPB} . $15\text{Na}_2\text{O}\cdot 85\text{SiO}_2$ depicts a 95% confidence interval to display accuracy of data collected. The three binary sodium silicate glasses have similar values of n_{TPB} , whereas Schott-8061 has a greater fatigue parameter, indicating a lower sensitivity to fatigue effects.¹⁴⁷

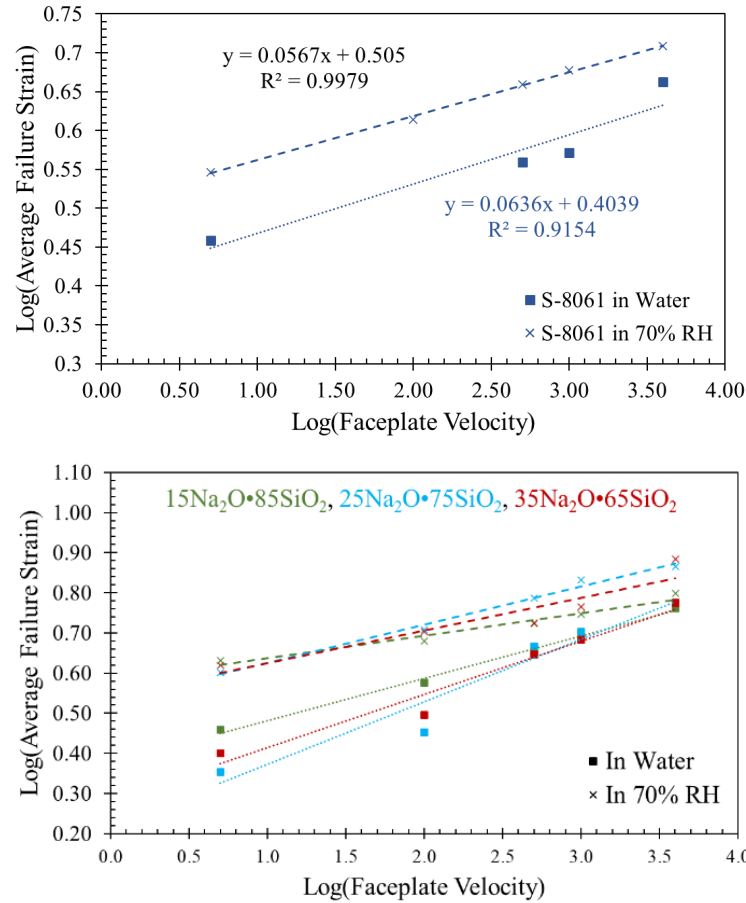


Figure 6-9: Dynamic fatigue graphs for glass fibers tested in 25°C DI water and 70% RH

Table 6-6: Summarized n_{TPB} for glass compositions from differing tests

	TPB in Water	TPB in 70% RH	DCB in 70% RH
15Na ₂ O•85SiO ₂	10.5	18.8	23.1 ± 1.3
25Na ₂ O•75SiO ₂	7.43	11.5	24.3 ± 1.7
35Na ₂ O•65SiO ₂	8.55	13.3	25.6 ± 0.96
Schott-8061	16.7	18.8	16.4 ± 0.54

6.3.6. Dynamic Mechanical Analysis

Figure 6-10 shows the results of the DMA experiments to measure the temperature-dependence of the mechanical loss modulus (at 2 Hz) for each of the three sodium silicate glasses. The glasses with 15 and 25 mol% Na₂O have similar loss peaks centered at approximately 225°C and both indicate a second loss feature that starts around 320°C, and another feature that apparently peaks below room temperature. The 35 mol% Na₂O glass has a peak at approximately 180°C, and a higher

temperature loss commencing at about 250°C but does not reveal an increased loss modulus around room temperature.

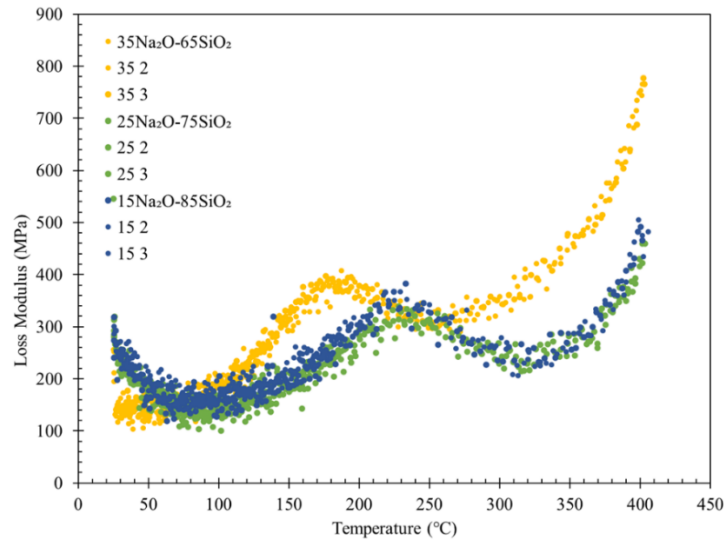


Figure 6-10: Temperature sweep conducted on sodium silicate glass series between 25-400°C

6.4. Discussion

A previous study done by Tang (Missouri S&T) found a dependence of failure strain on glass composition in sodium aluminosilicate glasses where an increase in alumina content decreased the susceptibility to fatigue. When analyzing the strain measurements for the binary sodium silicate glasses at different V_{fp} , there is not a clear compositional dependence on strain measurements. When comparing the compositions at fast faceplate velocities, they all have almost identical strain measurements. By using the power law comparison, Equation 6-7, Region I crack velocities can be empirically calculated. Figure 6-11 shows the predicted Region I crack velocities for each of the glasses. Similar to the dynamic fatigue slopes, the empirical slopes for the sodium silicate series are all similar to one another, whereas Schott-8061 glass has a greater slope.

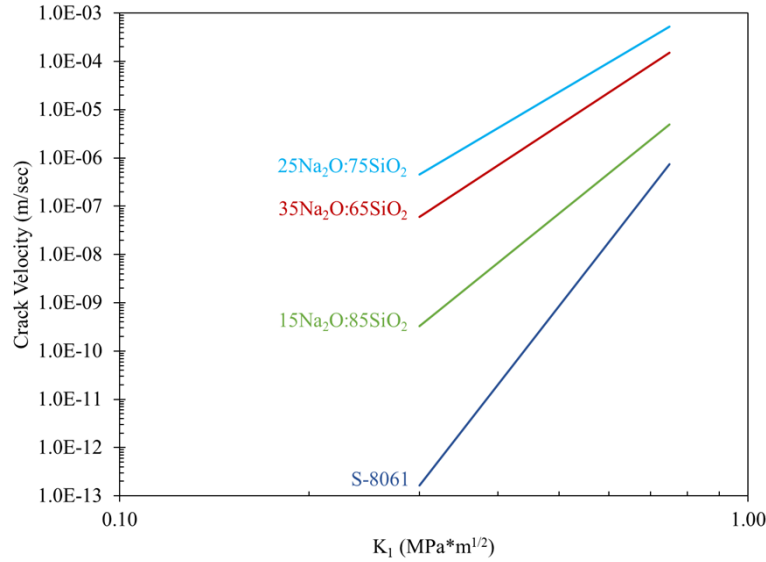


Figure 6-11: Empirically calculated region I crack velocities for alkali silicate glasses of study

Figure 6-12 compares the empirically calculated Region I crack velocities to the crack velocities measured with DCB. DCB measurements are depicted with markers, and the empirically calculated data is depicted as a line. Figure 6-12a depicts the data from the 15Na₂O•85SiO₂ composition, where there is a slight discrepancy between the measured and empirically calculated data. The measured data has a slope of 10.5 and the empirical data had a slope of 23.1. Figure 6-12b shows more agreement for the Schott-8061 samples, where the DCB data had a slope of 16.4 and the two-point empirical data had a slope of 16.7. Schott-8061 glass composition is made to be chemically robust, making it less susceptible to fatigue, whereas the binary sodium silicate structure has sodium ions and NBOs that tend to form silica rich regions within the glass. With a less structured glass, the glass becomes more susceptible to fatigue, especially in corrosive environments such as water.

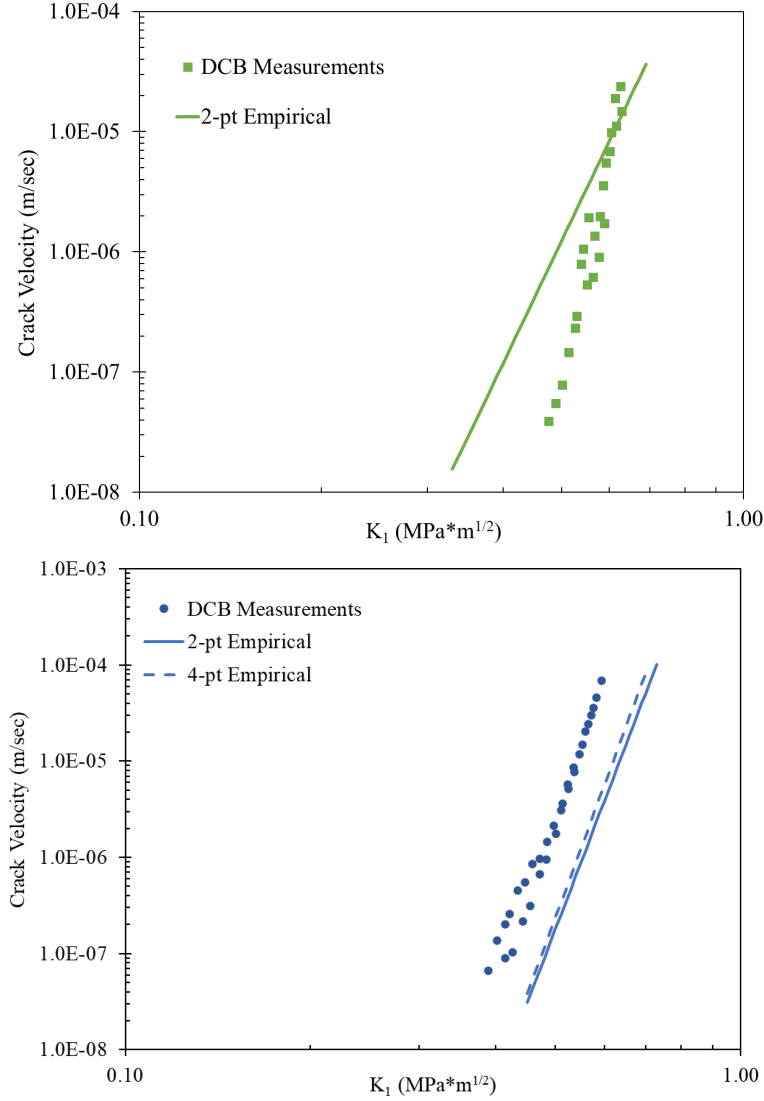


Figure 6-12: (a) K-V graph comparison for 15Na₂O•85SiO₂ composition, (b) K-V graph comparison for Schott-8061 glass for DCB, two-point, and four-point bending

6.3 Conclusion

DCB method was found to be beneficial for measuring stable crack growth in all three regions of subcritical crack growth. The 35Na₂O•65SiO₂ samples run in high humidity were found to halt crack growth due to the water penetrating and blunting the crack tip, however; when tested in 3% relative humidity, stable crack growth was observed. Two-point bend studies performed in DI water were able to produce consistent strain measurements and high Weibull moduli. Dynamic fatigue values calculated from two-point bend were used to empirically calculate Region I crack velocity, which agreed with analysis done on Schott-8061 for DCB and four-point bend. Mismatch in Region I crack velocity slopes in the sodium silicate series is likely due to mixed mechanisms taking affect during study.

7. GLASS SAMPLE DEVELOPMENT AND CHARACTERIZATION

7.1. Overview

Characterization and analysis of slow crack growth requires the development and synthesis of samples with stable cracks propagating under known loading conditions. In this projects, bibeam samples were generated based on mismatches in CTE between two different materials that enables stable crack growth. Challenges and protocols for generating these samples were explored for a new glass composition, sodium silicates. Additionally, fictive temperature was used for evaluation of changing glass structure for a single composition, as evaluated by FTIR. Finally, TOF-SIMS analysis was performed for evaluation of glass composition following crack growth. The results support understanding of the glass structure under varying conditions and developed samples for AFM analysis (in Section 8).

7.2. Bibeam Experiments

Bibeams were designed to impart a residual stress field on the glass of interest. This would allow for a crack to start from a notch and slowly move down the glass specimen over time. This is an ideal specimen for AFM experiments as there is no need for external loading sources to control the subcritical crack growth. Soda lime silicate glass bibeams were made using the procedures outlined by Grutzik *et. al.*¹⁴⁸. Additional bibeam designs were made for a variety of glasses outlined below.

7.2.1. Silica / Borosilicate

A fused quartz bibeam was designed to study the slow crack growth in amorphous SiO₂. The bibeam design consisted of fused quartz (GE124), borosilicate (Pyrex) and a glass adhesive tape (Vitta G-2571) to bond the borosilicate and fused quartz together. The glass tape was used to reduce the bonding temperature as to not impart too much stress. For the SLS bibeams, two SLS glasses were used with CTE difference of ~1ppm/°C. Fused quartz and borosilicate has a nominal CTE of 0.5 ppm/°C and 3.3 ppm/°C respectively. A lower temperature bonding process was required to reduce the stresses during bonding. A schematic of the bibeam dimensions is shown in Figure 7-1.

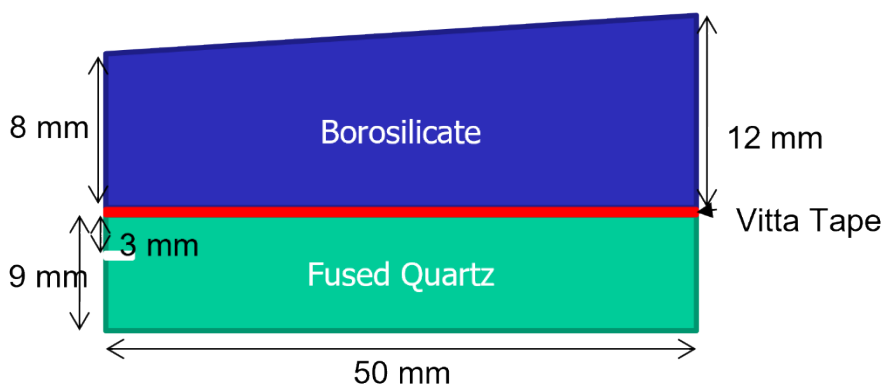


Figure 7-1: Schematic of borosilicate / fused quartz bibeam.

The borosilicate and fused quartz were first cut to size. A piece of the Vitta tape was then placed on the bonding surfaces of both glasses. The glass was then heated at 0.5 °C/min to 410 °C for 30 min. This was to debind the glass tape and form a layer of the sealing glass on the bonding surface. The

borosilicate and fused quartz were then stacked on top of each other and heated at 2 °C/min to 410 °C for 30 min.

7.2.2. Glass / Metal Epoxy bonding

A secondary bibeam method was explored to create bibeams. A method was adopted to from Grutzik *et. al*¹⁴⁹, where the glass is epoxy bonded to a steel beam. Rather than curing the epoxy at room temperature, if the epoxy is cured at an elevated temperature the glass will be under a constant residual stress field at room temperature. Schott S8061 glass was chosen with an aluminum beam and EPON 828 as the epoxy. Epicure 3140 was used as a curing agent. Figure 7-2 shows a schematic of the bibeam design.

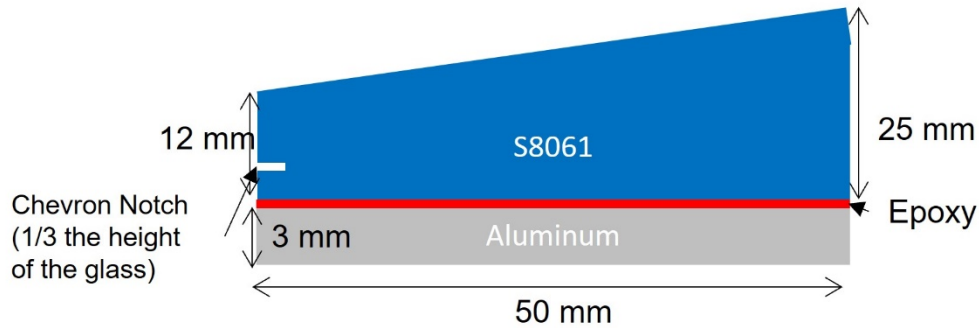


Figure 7-2: Schematic of glass epoxy bonded to aluminum bibeam design.

The glass and aluminum specimens were machined to the dimensions specified in the schematic with a chevron notch made in the glass. The epoxy:curing agent was mixed together at a weight ratio of 100:45. The mixture was mixed in a THINKY ARE-310 at 2000 rpm for 90 seconds and then at 2200 rpm for 180 seconds. The epoxy was then coated on the aluminum and a string was used to maintain a constant bond thickness. The glass was placed on the aluminum and a weight was used to maintain a load during the curing process. The beam and fixturing was placed in a vacuum oven at 50 °C and left overnight.

7.2.3. Sodium silicates / Glass-Ceramic

A diffusion bonded bibeam approach, similar to the SLS glass, was taken for the sodium silicate glasses. A trial bibeam was fabricated using the 35Na65Si glass bonded to a BPS16 glass ceramic. Additional samples were fabricated (Table 6-2).

7.3. Fictive Temperature Control

Experiments were planned to control the fictive temperature necessary to make bibeams. The fictive temperature of fused quartz can be controlled either by annealing for long periods of time near the T_g^{150} or by quenching from temperatures above $T_g^{151-152}$. To verify the fictive temperature of the glass changed with quenching, FTIR can be used to verify changes in the structure of the glass by measuring the peak position at $\sim 1120 \text{ cm}^{-1}$.¹⁵⁰⁻¹⁵¹ A quenching apparatus was constructed, and the quenched glass measured in FTIR.

7.3.1. Quenching apparatus

A vertical split tube MoSi_2 furnace was used to quench the fused quartz (GE-124). The fused quartz was 25x25x3 mm in dimension and would hang from a platinum wire in the hot zone of the

furnace. The glass was heated at 10 °C/min to 1200, 1300, 1400 or 1500 °C and held for 15 min to equilibrate. The platinum wire would then be released, and the glass would fall into a DI water bath. Figure 7-3 shows an image of the setup.

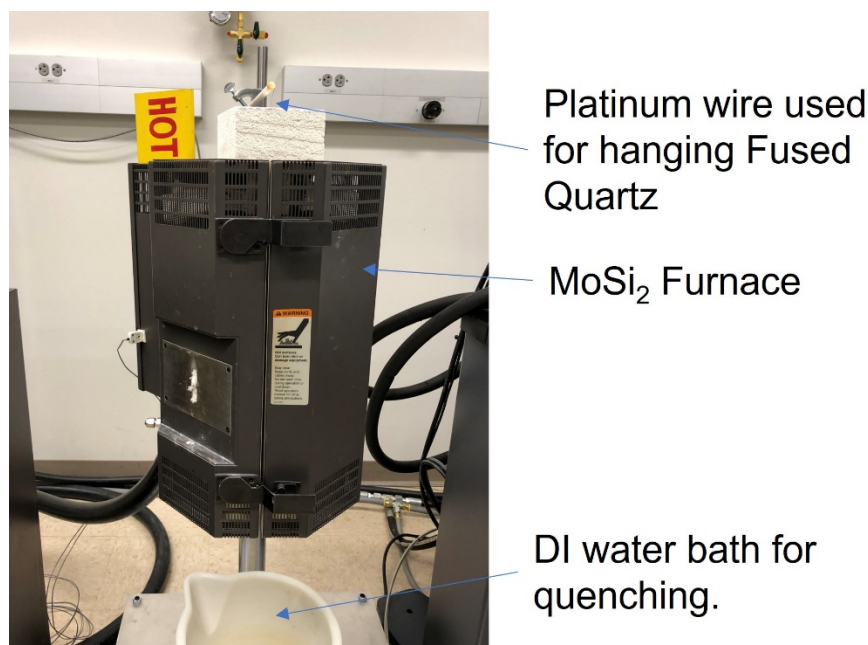


Figure 7-3: Quenching setup

7.3.2. FTIR

A Thermo Nicolet 6700 spectrometer was used to characterize the fictive temperature of the fused quartz. Samples were scanned in transmission mode from 4000 to 400 cm⁻¹ at a step size of 2 cm⁻¹. Origin labs was used to fit the peaks of the spectrum with a Gaussian-Lorentz fit.

7.4. ToF-SIMS

ToF-SIMS (Time-of-Flight Secondary ion Mass Spectrometry) was used to determine relative Na thickness on the fracture surface. After fracturing, the two halves were placed in a mount designed to hold them level and parallel to the sample holder surface. Initially, images were attempted across the entirety of the fracture surface, but it was found that unevenness of the fracture brought the immediate analytical area in and out of the analytical plane, making direct imaging over large areas impossible.

Additionally, the Na thin surface film was thick enough to prevent the analysis glass substrate signals such as Si⁺, making relative concentration determinations impossible. Therefore, it was decided that a series of depth profiles, designed to measure the relative Na film thickness, would be performed across the fracture surface instead. In this experiment, depth profiles spaced 2mm apart were acquired. Using an Ion-TOF ToF-SIMS.5 (Munster, Germany, www.iontof.com), depth profiles were performed. An interlaced Bi¹⁺ HC-BUNCHED 25kV pulsed beam rastered over 50x50μm² and 100nA, 600x600μm² 1kV Xe was used to perform the analysis. Bi¹⁺ was the analytical probe while Xe was used to remove material. The Na₂⁺ ion was used to track Na because the Na⁺ signal saturated. The substrate was followed using the Si⁺ ion. Because of differing sensitivities, a correction factor of 4 was applied to the Na₂⁺ signal. Resulting Na₂⁺ / (Si⁺ + Na₂⁺) and Si⁺ / (Si⁺ + Na₂⁺) plots were made versus sputter ion dose.

7.5. Results

7.5.1. *Bibeams*

In the first iteration of the fused quartz/borosilicate bibeam the specimen bonded together well (Figure 7-4). However, the size of the borosilicate glass was not the correct size needed for the propagating a steady crack. In the second iteration (Figure 7-4) both the borosilicate and fused quartz cracked after the bonding process. It is likely due to the large CTE mismatch between the borosilicate and fused quartz. A lower CTE glass than borosilicate does not exist. Due to this and the complications of this design was sidelined to pursue the epoxy bonded specimens.

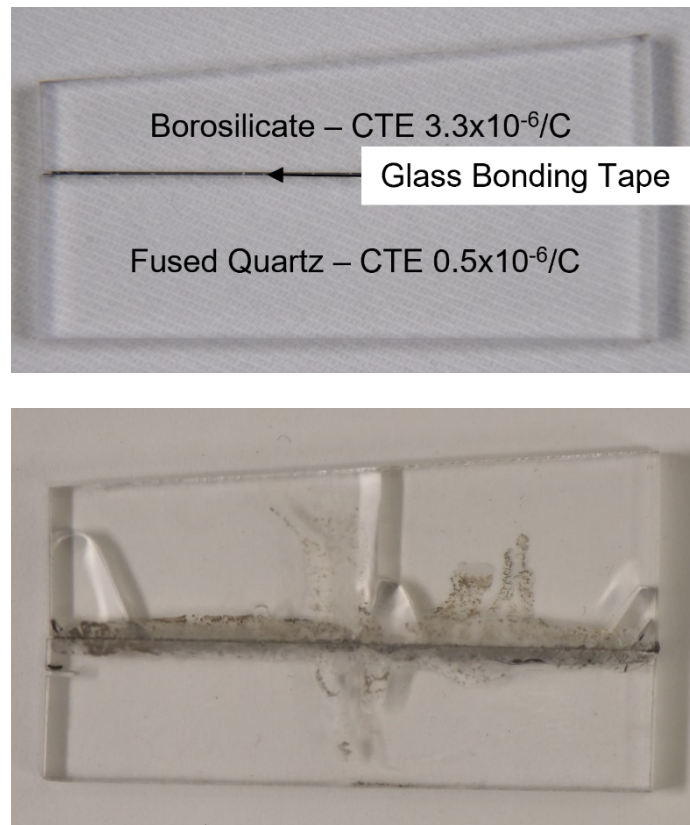


Figure 7-4: Fused quartz / borosilicate bibeam with (top) smaller borosilicate specimen and (bottom) larger borosilicate specimen with cracks.

Figure 7-5 shows an image of the S8061 glass epoxy bonded to the aluminum beam. Some pores were present in the epoxy bonding but otherwise the process worked well. However, a crack never propagated from the notch. The specimen was placed in liquid water for up to a month to try and promote crack growth, but it never occurred. When looking at the specimen in cross polarized light (Figure 7-5.b) it appears as though there is not much stress in the glass. It is unknown why the stresses did not translate as predicted by simulations. Due to these complications the epoxy bonding process was sidelined to pursue diffusion bonding of sodium silicate samples.

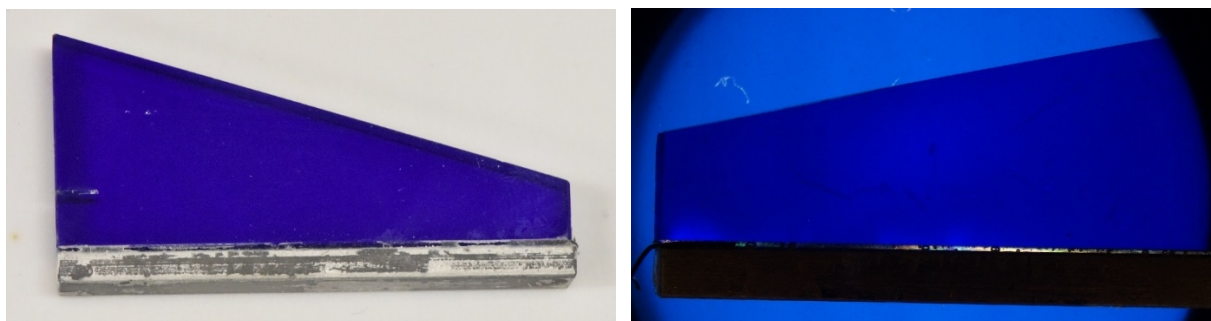


Figure 7-5: Image of S8061/Aluminum bibeam (left) in white light and (right) under cross polarized light.

A proof-of-concept bond was conducted between the 35Na65Si sodium silicate and BPS16 glass-ceramic, which has a nominal CTE of 15.3 and 16 ppm/°C respectively. A small bar (~3x3x20 mm) of the 35Na65Si glass and BPS16 were polished to a mirror finish with iterative grinding of SiC paper and a 0.5 μm CeO slurry for the final polishing step. The specimens were placed on top with a steel block on top for weight. The specimens were heated to 25 °C above the T_g of the 35Na65Si glass (475 °C) for 20 hours. Figure 7-6 shows the resulting specimen in cross-polarized light. The specimens bonded together well, with no cracks and a uniform stress field across the Na-silicate specimen. Specimens of the three glass compositions and glass-ceramics were machined for bibeam bonding (Table 6-2). Due to time constraints the specimen bonding were not completed.

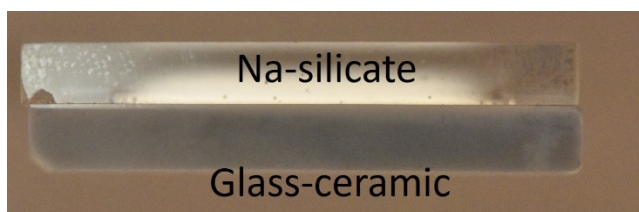


Figure 7-6: Image of sodium silicate / glass-ceramic bibeam under cross polarized light.

7.5.2. Fictive Temperature

Figure 7-7 shows the FTIR plot with the characteristic peak for Si-O-Si stretching vibrational node at 1120 cm^{-1} . The green lines indicated the deconvoluted peak fits for identifying the peak position. Figure 7-8 shows the fitted peak positions for 1200 and 1400 °C quenches. The 1400 °C has a lower wavenumber than the 1200 °C quench sample, which aligns with past work indicating the higher the fictive temperature the lower the 1120 cm^{-1} peak position.¹⁵⁰⁻¹⁵¹ The other quenched samples did not follow this trend well, but it was noticed that the surfaces were “hazy” likely due to crystallization of the fused quartz which may have interfered with the measurements. A better approach to avoid crystallization would be to lower the glass sample into the furnace at temperature for a short period of time before quenching. This would eliminate the long heating times and likely avoid crystallization. These experiments were sidelined to focus on the sodium-silicate glass work.

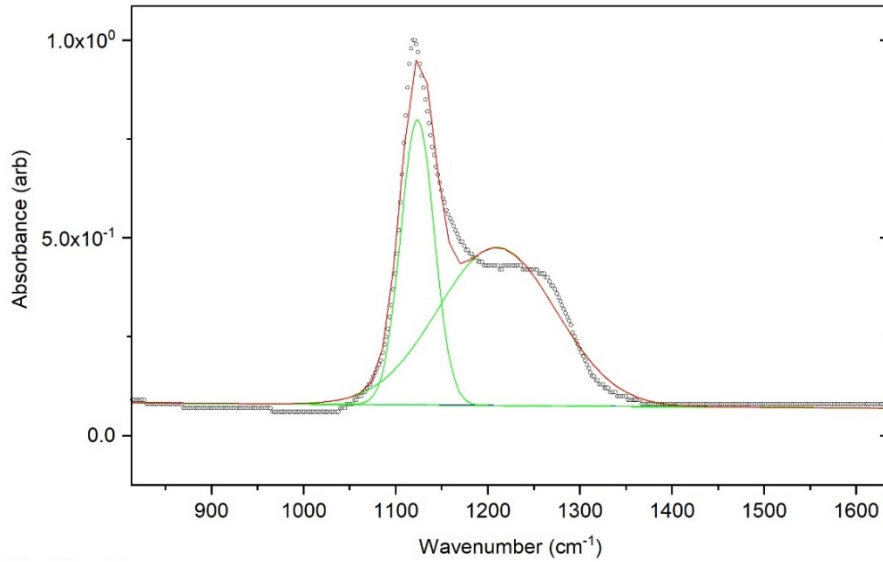


Figure 7-7: FTIR spectrum of fused quartz with peak fitting analysis.

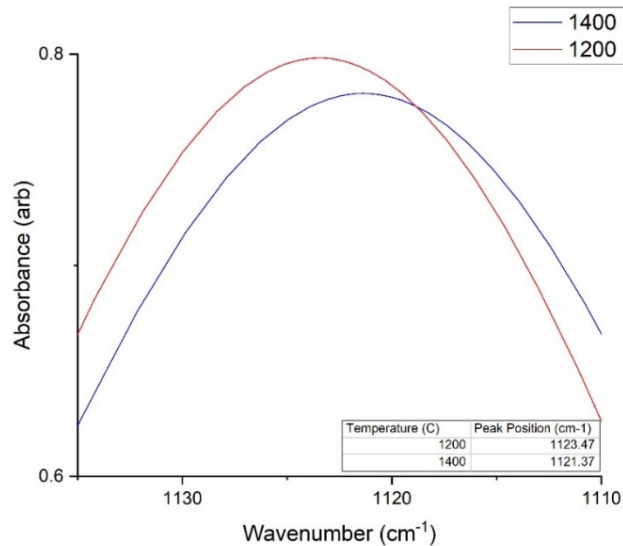


Figure 7-8: FTIR fit of 1200 and 1400 °C quenches showing the shift in the 1120 cm⁻¹ peak.

7.5.3. ToF-SIMS

The crossover points for the Na₂⁺ and Si⁺ signals in the preceding plots were used to consistently determine the relative thickness of each profile location's Na layer. Relative Na thickness versus profile position was then plotted (Figure 7-9). The crossover point was then used to determine a relative Na thickness on the fracture surface of the glass specimen. Figure 7-10 shows the relative depth of the Na with respect to the sample position. The lower sample positions were testing at slow crack velocities (Region I) whereas the higher sample positions were tested at higher crack velocities (Region II). No obvious change in the sodium depth is observed. Although we cannot observe a difference along the fracture surface, there is a sodium depth profile which has been suggested by previous work.¹⁵³⁻¹⁵⁴ Future experiments comparing the different sodium silicate glasses would be interesting to note a change in the Na thickness layer on the fracture surface. Due to time constraints these experiments could not be completed.

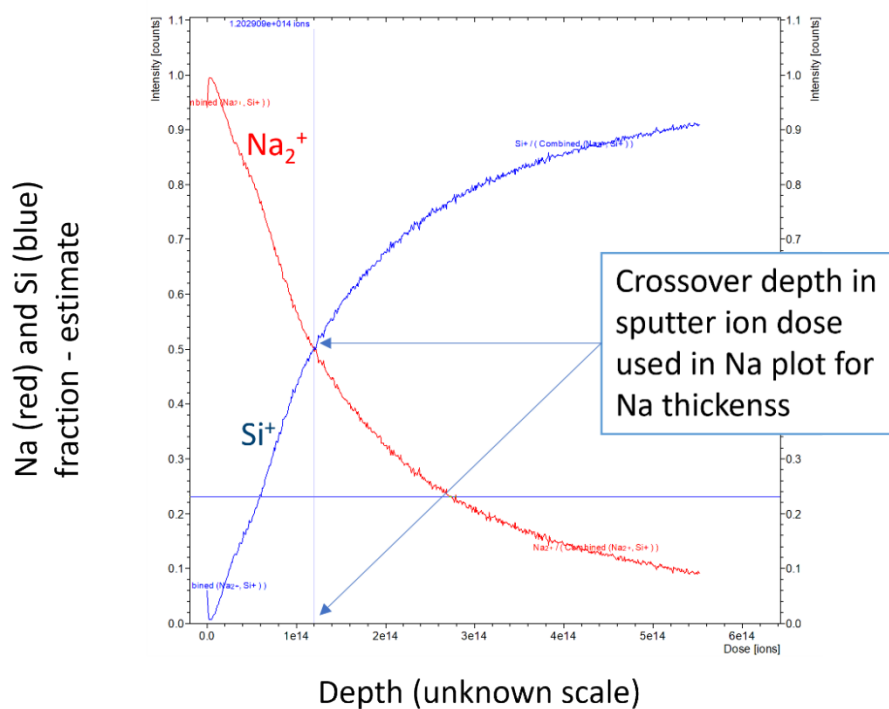


Figure 7-9: ToF-SIMS depth profile of the relative Si^+ and Na_2^+ ions of the 35Na65Si glass.

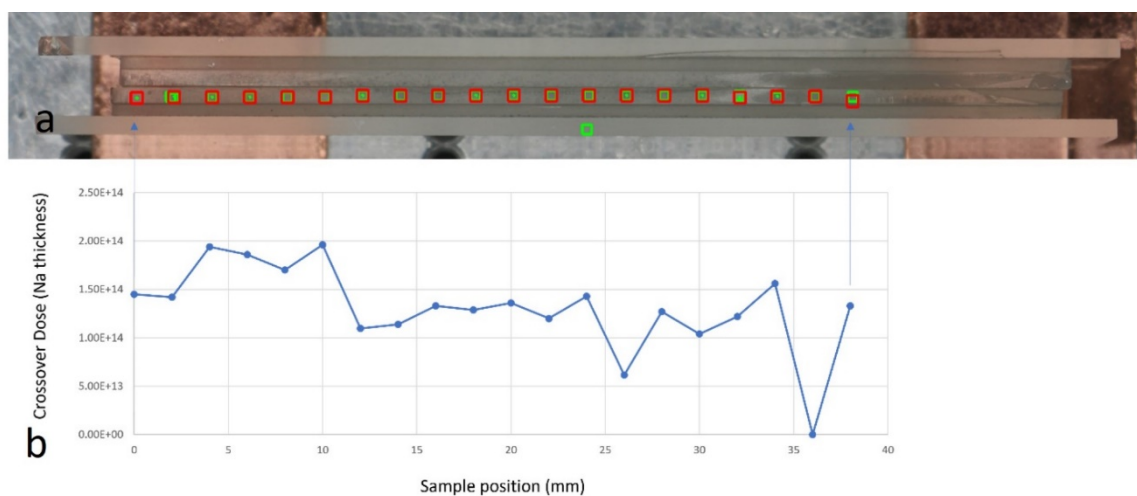


Figure 7-10: a) Image of sample used for ToF-SIMS analysis with locations of the scans associate with b) relative cross-over point of the specified location.

8. AFM FOR FRACTURE STUDIES

8.1. Overview

Atomic force microscopy was used to visualize and measure slow crack propagation in sodium lime silicate samples. Using large-sample AFM systems with specialized tips and scanners, fractures less than 20 nm wide and a few nm deep were measured as a function of relative humidity. Continuous scanning and image capture over periods of several days allowed the determination of the crack tip velocity. The dependence of crack tip velocity on relative humidity was measured by enclosing the sample and AFM head in a humidity-controlled chamber. The crack tip velocity was measured as low 3.99×10^{-12} m/s at 15% RH and as high as 3.68×10^{-10} m/s at 40% RH.

8.2. Introduction

With nanometer-scale resolution, AFM is well-suited for imaging cracks and related surface topography in brittle materials. In AFM, an etched silicon probe - sharpened to a tip radius that can be as small as a few nanometers – is scanned in near-contact to a sample surface and traces out surface topography in three dimensions. Because of the precise control of the tip location, as well as the size of the tip, the AFM can image the structure of the crack in much greater detail than techniques using light optics. In addition, the AFM's ability to image insulating samples without modification (e.g., depositing conductive films to use SEM) enables the study of crack tip dynamics over time.

Figure 8-1 shows two AFM images at different magnifications of the same crack tip as it propagates in a sodium lime silicate bi-beam sample.¹⁵⁵⁻¹⁵⁶ The crack appears as a trench less than 1 μm wide with raised features adjacent to the trench. While other groups have shown AFM images where the glass fractures appear mainly as trenches^{28, 85}, we have found that the appearance of the crack is highly dependent on sample preparation method, sample cleanliness, and the RH of the environment surrounding the sample during AFM image acquisition.

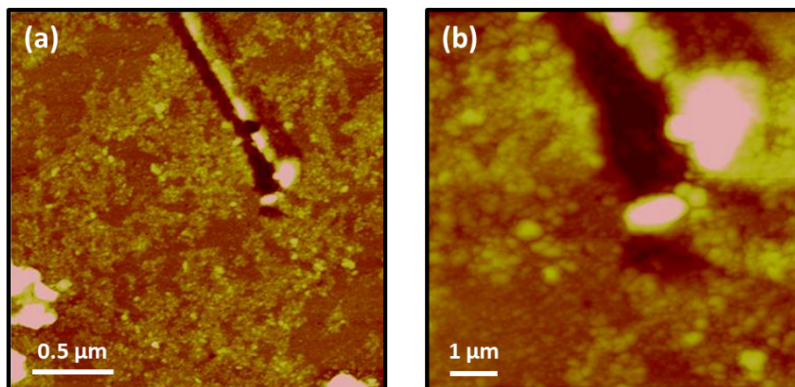


Figure 8-1: AFM images of a sodium lime silicate bi-beam glass sample. The dark, linear feature near the top of the image is the intentionally initiated crack in the glass sample. The raised features along the crack are believed to be humidity-related, while the residue on the surrounding plateau is residue on the sample surface.

8.3. AFM Tip Selection

Four different high resolution AFM probes were evaluated by imaging the same crack tip formed in a glass indent sample. Two of these tips were monolithic etched Si probes (NANOSENSORS SSS-NCH & Bruker TESP-HAR), and two of the tips were etched Si probes w/ diamond-like carbon (DLC) “extra-tips” (BudgetSensors SHR300 and Mikromasch HiRes-C). The

SEM images in Figure 8-2 show the Hi'Res-C AFM tip. Figure 8-2.b shows a close-up image of the tip.

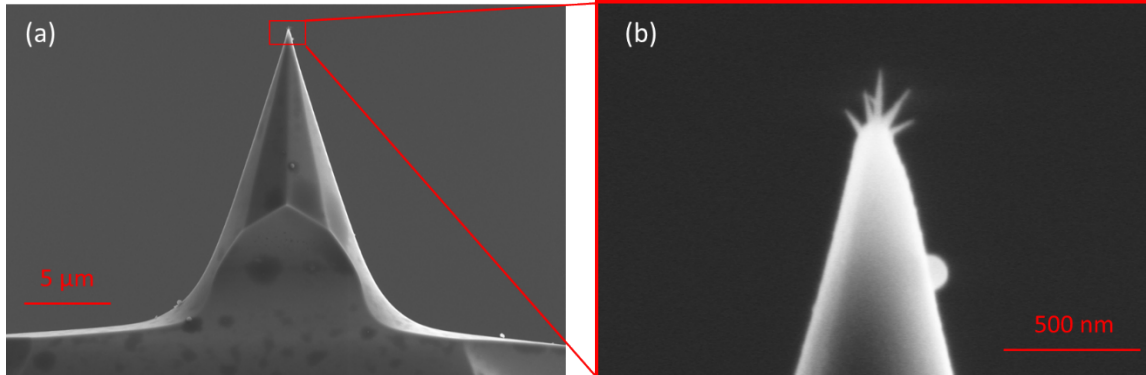


Figure 8-2: SEM images of one of the two AFM tips that had diamond-like carbon whiskers attached to the end of the probe tip to improve resolution of the AFM measurement. The “extra-tip” whiskers can be clearly seen in (b) and had the tendency to break off while scanning over the glass crack topography.

where diamond-like carbon extra-tips are extending from the end of the etched Si tip. These extra-tips are used to improve the geometry of the AFM probe tip so that higher resolution images can be acquired with the top-most, sharp whisker. While the resolving ability of this type of probe was exceptional, imaging could only be accomplished after multiple attempts, having to install a new tip after each attempt. The monolithic AFM tips, such as the NANOSENSORS SSS-NCH tip shown in Figure 8-3, however, did not need multiple new tips to acquire a high-quality image. It was determined that the probes that had “extra-tips” on them were not stable and that these tips had the tendency to break off after imaging only a few minutes. Presumably, scanning these tips over the crack trenches introduced too much topography, which resulted in an excessive lateral force on the DLC whiskers.

The monolithic Si probes, such as the NANOSENSORS SSS-NCH shown in Figure 8-4, did not have the high frequency of scan-related wear that the probes with DLC whiskers did. Therefore, after an initial survey to evaluate the four different AFM tips, the remainder of the research outlined in this report was conducted using the NANOSENSORS probe, which had the sharpest tip of the two monolithic probes.

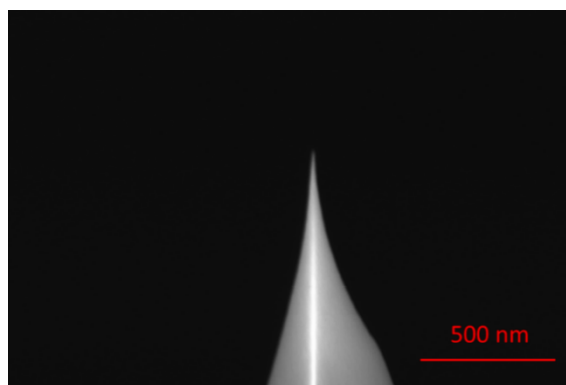


Figure 8-3: SEM image of the end of a NANOSENSORS SSS-NCH tip. This monolithic Si AFM tip was used exclusively for the work presented in this report (tip radius ~2 nm).

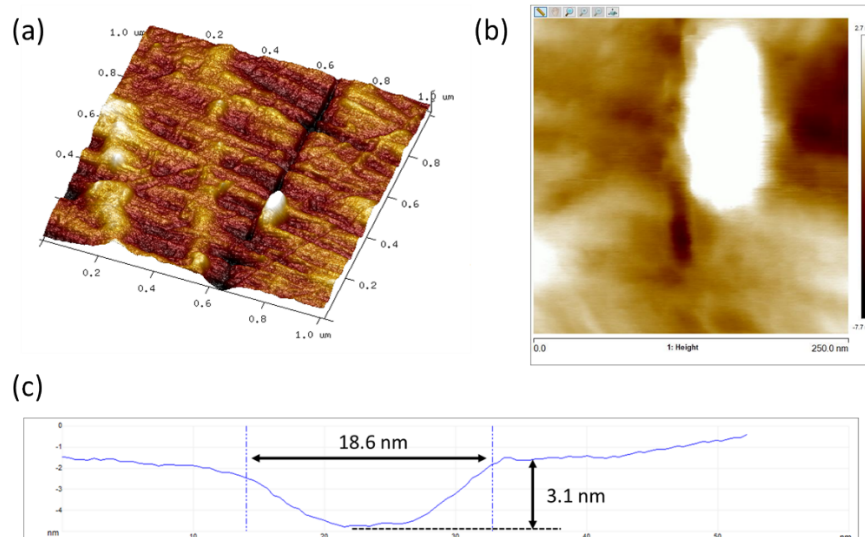


Figure 8-4: AFM data of a crack in a sodium lime silicate bi-beam sample displayed (a) in 3D and (b) in 2D. The cross-sectional line was taken from the AFM data shown in Figure 8-4.b

Figure 8-4 shows data acquired on a crack in a sodium lime silicate glass sample. Figure 8-4.a shows a three-dimensional rendering of the AFM data, where a raised feature (white contrast) appears near the tip of the crack (seen more clearly in the two-dimensional image in Figure 8-4.b). A cross-sectional line trace extracted from the data is seen in Figure 8-4.c, showing that the crack has a width of 18.6 nm and a depth of 3.1 nm.

8.4. Fiducials

Some preliminary work, using a FIB, was performed on glass samples to explore the use of fiducial markings to assist locating crack tips and to use as a reference to track relative movement of the crack tips to measure crack tip velocities. The schematic drawing in Figure 8-5 shows how a FIB is used to deposit material in a controlled manner.

Ion Beam Induced Deposition

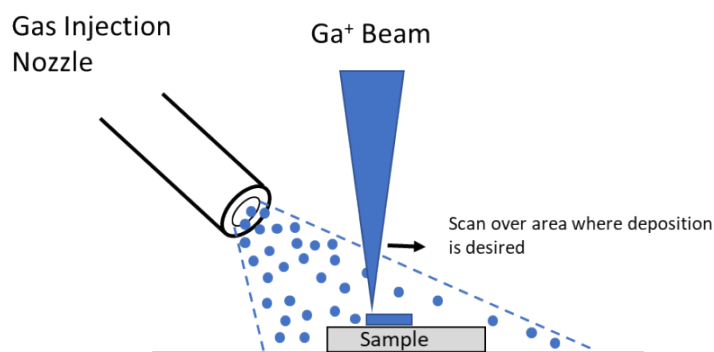


Figure 8-5: Schematic drawing showing the use of focused ion beam deposition to create fiducial markings on the glass samples.

The optical images in Figure 8-6 show an array of tungsten squares that were deposited on a glass slide. The goal with this deposition strategy was to produce markings that could be seen by both

the optical microscope, as well as the AFM. This would allow any captured AFM images to have a reference structure in the AFM image that could be easily related to a low-magnification optical image that shows a larger distance. Because one of the goals of this project was to measure crack-tip velocity with the AFM, this was originally believed to be a key experimental need.

Once this process was demonstrated and optimized on a glass slide, FIB fiducials were deposited on a glass sample with a crack initiated into it. The optical images in Figure 8-6 were taken from the optical navigation camera of the VEECO Dimension 5000 AFM used for this project. The image in Figure 8-7.a was taken with the fiducials in focus (AFM tip raised), while the image in Figure 8-7.b was taken after the tip was lowered into imaging position, just above the sample surface.

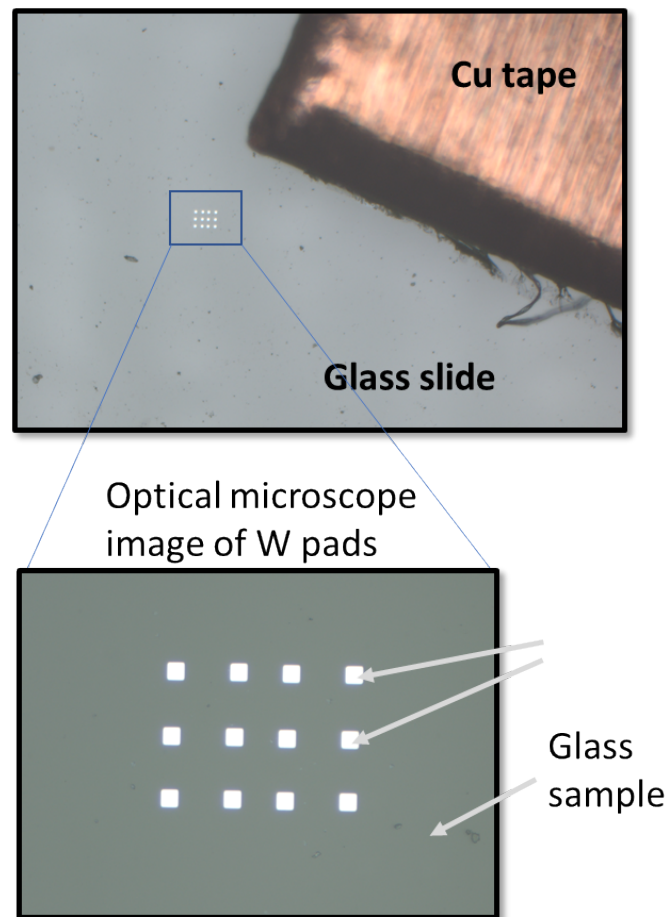


Figure 8-6: Optical microscope images of FIB-deposited tungsten fiducial markings on a glass slide.

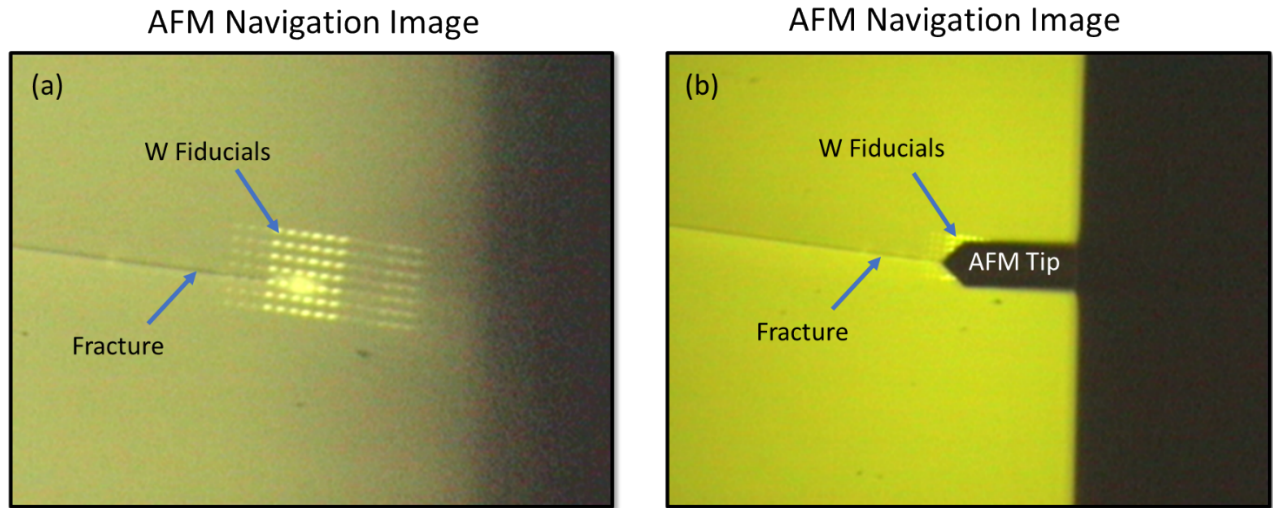


Figure 8-7: Optical images taken from the AFM navigation camera with (a) the tip raised and camera focused on the sample surface, and with (b) the tip lowered and scanning the crack tip plus fiducials.

The AFM image in Figure 8-8 shows the array of tungsten fiducials in the vicinity of the crack tip. This sample highlighted the potential difficulty of having fiducials in a location where the crack tip might want to propagate and, subsequently, interfering with its movement. It was later discovered the surface topography near the crack tip, as imaged by the AFM, was unique enough to use as a fiducial. Therefore, it was decided to not use FIB-deposited fiducials for the remainder of the study.

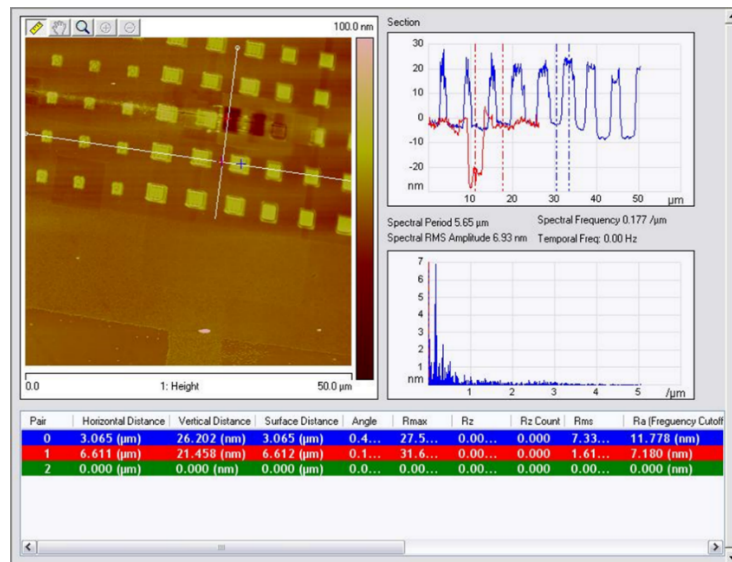


Figure 8-8: AFM image and accompanying cross-sectional analysis of tungsten fiducials in the vicinity of the crack tip on a glass bi-beam sample.

8.5. Four-point Bend Stage

A four-point bend stage was also used to conduct AFM studies as a function of constant load. Figure 8-9 shows a photograph of the experimental set-up, which included the use of a “High Aspect

Ratio” VEECO D5000 AFM head. This specialized AFM head does not use a standard tip holder; instead, a bead of wax is used to mount the AFM tip so that the assembly can fit into tight geometries. The usual AFM camera needed to be removed to allow the use of the bend stage. A USB camera was used in place to allow navigation and placement of the AFM tip onto the sample surface.

This experimental configuration was just to image long bars of Schott-8061 that were indented with a Vicker’s indenter to initiate a crack. Once a crack was initiated into the sample, it was loaded into the four-point bend stage to study the effect that a static load has on crack tip velocity. As an example of this imaging capability, the series of AFM images in Figure 8-10 show the blue glass surface with three different loads applied: (a) 1 N, (b) 10 N, and (c) 25 N. Interestingly, after increasing the load above 10 N, new surface topography could be seen in Figures 8-10.b and 7-10.c. It is unclear if this is due to relieving stress imparted into the sample, or if another phenomenon causes this – further study was only conducted on a limited basis, as this was not a direct focus of the project. Moreover, loads up to 40 N were applied, but the crack tip was not observed to move. The sample eventually snapped before any crack propagation was observed.

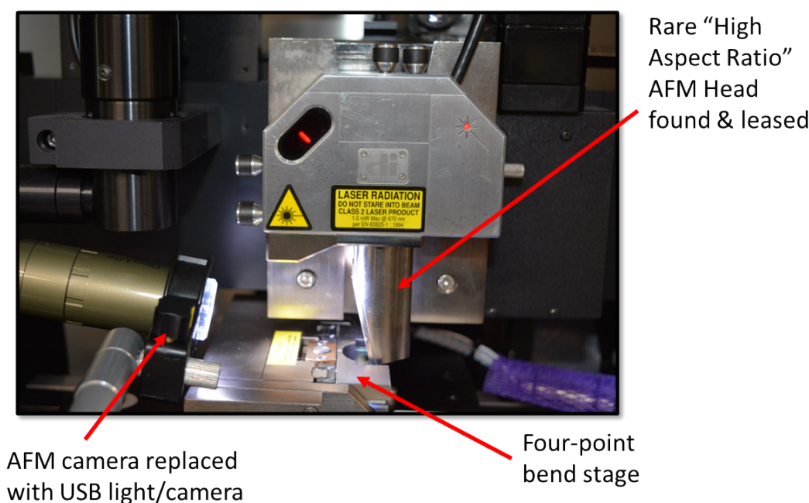


Figure 8-9: Photograph showing the four-point bend stage integrated into a VEECO D5000 AFM system. The standard AFM head was replaced with a specialized, high-aspect ratio head, and the standard navigation camera was replaced with a compact USB camera to enable the AFM tip to reach a sample in the stage.

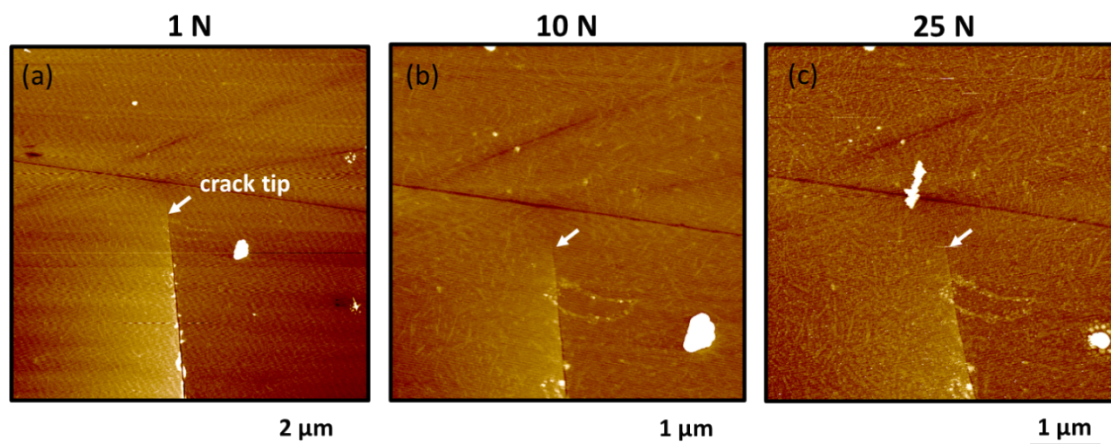


Figure 8-10: Series of AFM images of the same crack tip as the four-point bend stage load was increased from (a) 1 N to (b) 10 N to (c) 25 N. The crack tip was not observed to move, but new vertical surface features were seen at (b) 10 N and (c) 25 N. This blue glass sample was prepared using a Vicker's indenter to initiate a crack in the surface.

8.6. AFM Measurement of Crack Tip Velocity

The AFM was eventually successful in measuring crack tip velocities in the study of soda lime silicate bi-beam samples that were stored in a humidity chamber. The series of AFM images in Figure 8-11 were magnified so the pixilation could be seen and, subsequently, distances could be measured by counting pixels. What is clear in all three images is that there are surface features nearby the crack tip to use as a reference point, illustrating how deposited fiducials are not necessary. The horizontal white line aligns with the tip of the crack, while the red line aligns with the top of the round feature that was used as a fiducial. Over the course of 9200 sec, the white line moves from four pixels below the red line (a) to two pixels past the red line. Plotting these data in Figure 8-11 and fitting a line yielded the velocity (slope) of 4×10^{-12} m/s.

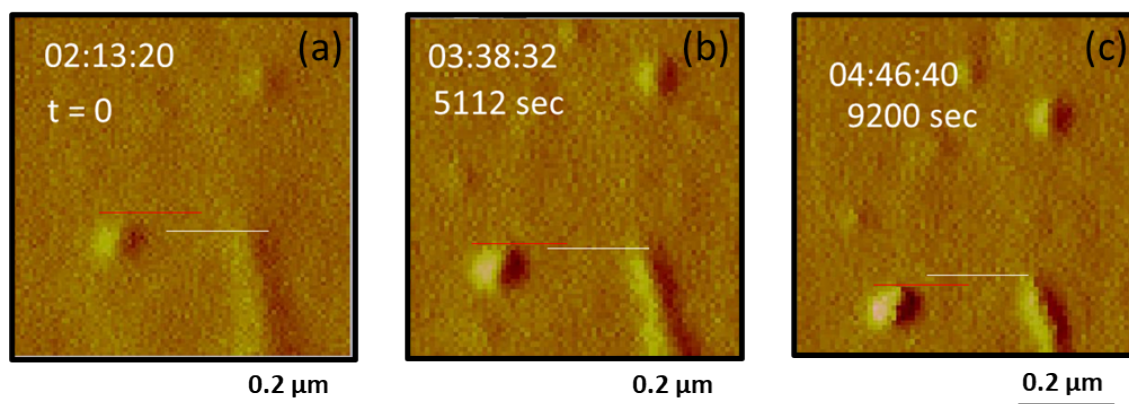


Figure 8-11: Series of AFM images from a glass bi-beam sample. The horizontal lines are drawn to assist in measuring the progress of the crack propagation relative to a fixed fiducial.

Tip Location vs. Time (ambient ~20% RH)

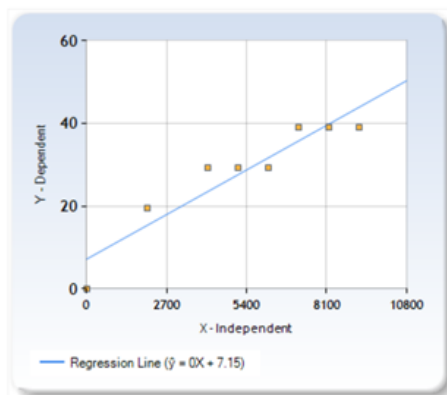


Figure 8-12: Plot of the AFM data (partially shown in Figure 8-11) showing the distance moved (y-axis) as a function of time (x-axis). The linear regression of this data yields a slope of 3.99×10^{-12} m/s, which is the measured crack tip velocity for this sample.

8.7. Crack Tip Imaging – Tip Recession

The AFM data shown in Figure 8-13 shows the progression of a crack tip moving in reverse. Using a similar analysis to what was shown in Figures 8-11 and Figure 8-12, a recession rate was calculated in Figure 8-13 of -26.9×10^{-12} m/s. While the direction that the crack tip moved gives the appearance that the crack is closing, the AFM data suggest that this is due to the sample surface drying. This theory was tested by placing a drop of deionized water on the crack tip. At first, the crack appeared as a raised feature and, as the water evaporated from the surface, the height of this raised feature diminished, while the apparent location of the crack tip (raised feature) moved away from the true crack tip (depressed feature). What appeared to be movement of the crack tip, we postulate, was simply the moisture evaporating from the end of the crack.

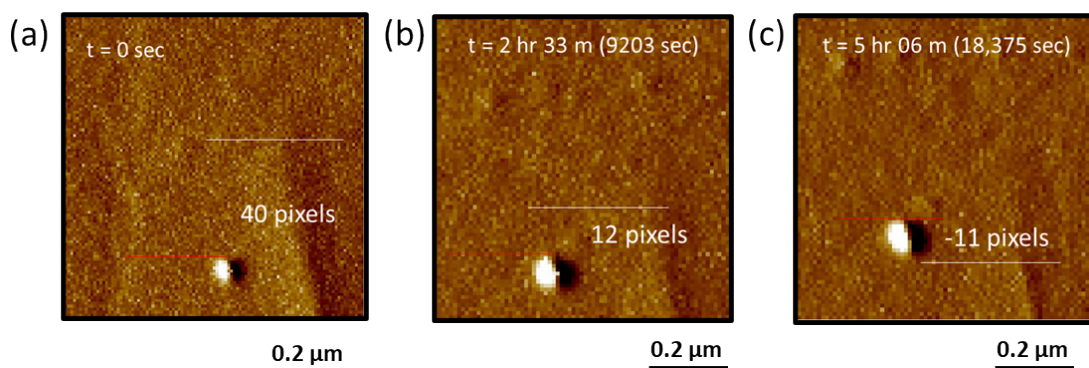


Figure 8-13: Series of AFM images taken after the glass bi-beam sample was removed from storage in a humidity box maintained at 75% RH. Over the course of several hours, the crack tip appeared to recess.

Recession rate (during first 5 hrs) = -26.9×10^{-12} m/sec
(ambient $\sim 20\%$ RH)

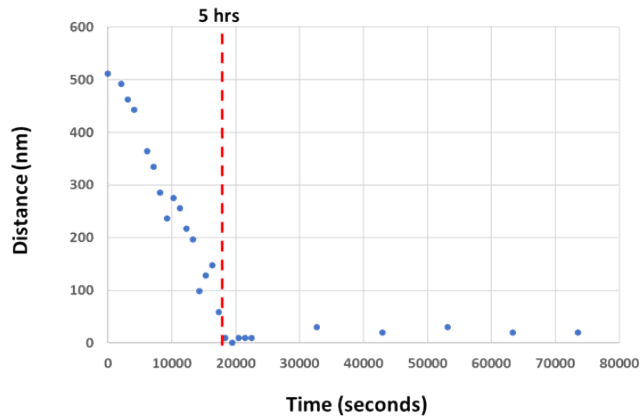


Figure 8-14: Plot of the AFM data partially shown in Figure 8-13. The distance the crack tip was measured to move (y-axis) is plotted as a function of time (x-axis). The calculated crack tip velocity was -26.9×10^{-12} m/s.

8.8. AFM Measurement of Crack Tip Velocity versus Relative Humidity

The crack tip velocity was measured as a function of relative humidity using AFM. A sodium lime silicate bi-beam sample was stored in a 75% RH humidity chamber after initiating a crack by sawing a notch. The sample was stored in the humidity chamber but removed to measure crack tip movement using a light optical microscope. The plot in Figure 8-15 shows the movement of the crack tip over a several month period, as well as the time range when AFM measurements were acquired. The goal of storing this sample at 75% RH was to accelerate the crack propagation, through exposure to moisture, until the tip velocity began to slow down to the range where AFM measurements would be reasonable to track. The slow scan speed of the AFM (~ 30 minutes to acquire an image), as well as its limited scan range ($\sim 100 \mu\text{m}$), required a tip velocity that did not result in the crack tip moving outside the AFM scan window for several hours.

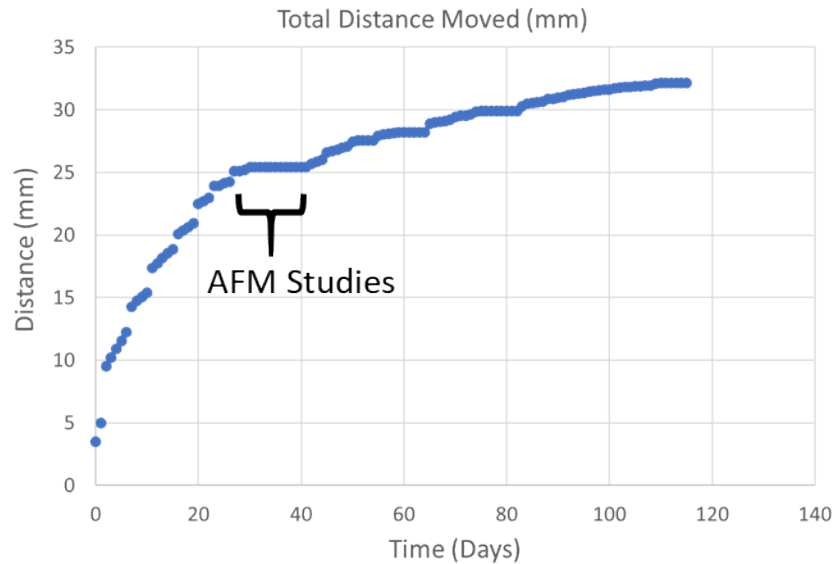


Figure 8-15: Plot showing the total distance the crack tip in a sodium lime silicate bi-beam sample moved over a period of several months, as measured by an optical microscope. The time range labeled “AFM Studies” denotes when the sample was removed from storage in a humidity chamber with 75% RH and placed in the AFM. For AFM imaging, the sample and AFM head was enclosed in a humidity-controlled volume with a hygrometer to monitor relative humidity.

Crack tip imaging on the bi-beam sample was performed using a large sample AFM (VEECO D5000) with the standard AFM stage and scanner. The entire AFM head and sample were enclosed in a plastic environmental enclosure equipped with a humidity source. A digital hygrometer was positioned next to the sample and AFM tip, and the relative humidity was monitored while the images were captured. Once the crack tip was located and the AFM stabilized, images were continuously captured over several days. The image pixel resolution was 512 x 512, and the tip was scanned at a rate such that each image took 28 min to capture. Figure 8-16 shows a series of AFM images that were captured over a ~4 day period where the RH was 23%-25%. The raised feature extending upwards from the bottom of the image is the fracture in the glass. The measurements shown on these images were taken relative to the raised cluster seen adjacent to the fracture. This series of images demonstrate that over a period of several days, the sample surface remained relatively unchanged, except for the location of the crack tip.

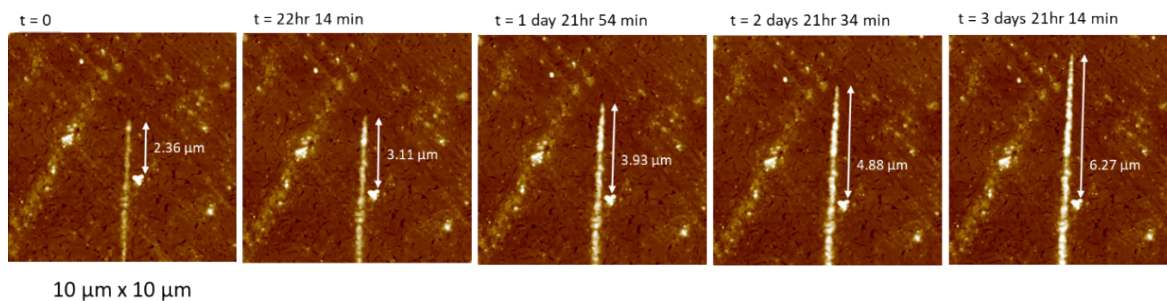


Figure 8-16: Series of AFM images showing the propagation of the crack tip in a sodium lime silicate bi-beam sample while imaging in a humidity-controlled environment. The RH was held between 23% and 25% over the course of this image series.

The distance the crack tip traveled was plotted as a function of time, and the resulting graph is shown in Figure 8-17. The linearity of the data allows a simple linear fit to the data for extracting the slope of the data, which corresponds to the crack tip velocity. Figure 8-17 shows that the data follows two different lines with different slopes; after review of the hygrometer readings, it was found that the humidity drifted from 23% to 25% over the time this data was acquired, and so the increase in crack tip velocity from 9.5×10^{-12} m/s to 15.2×10^{-12} m/s is attributed to the increase in humidity.

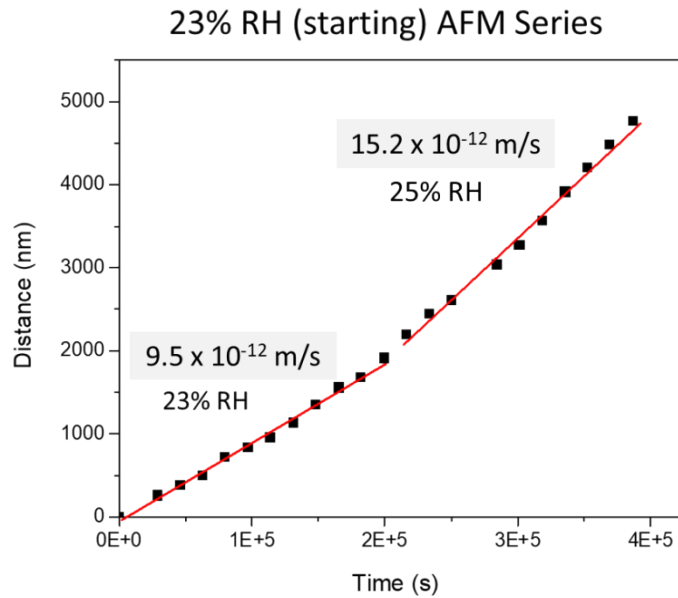


Figure 8-17: Plot showing the distance the crack tip moved as a function of time. The linearity of the data allows a simple linear regression to extract the slope, which corresponds to the crack tip velocity.

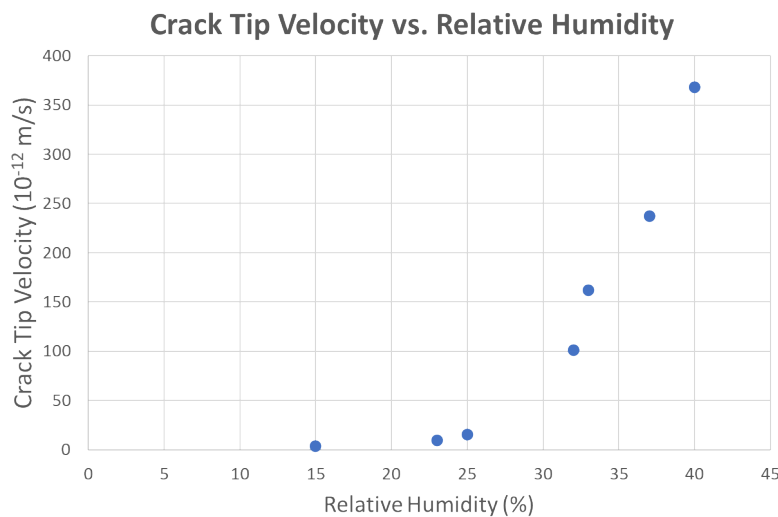


Figure 8-18: Plot showing the crack tip velocity, as measured by AFM, as a function of increasing relative humidity.

The analysis shown in Figures 8-16 and 8-17 was repeated on the same sample for a range of RH values up to 40%, and the results are shown in Figure 8-18. This plot shows that the crack tip velocity on the bi-beam samples has a strong dependence on the humidity. While this is not surprising, the ability to measure the crack tip velocity at the lower end of the humidity scale demonstrates that AFM is a powerful technique for glass fracture studies.

8.9. Summary/Conclusions

Atomic force microscopy was successfully used to measure crack tip velocities of sodium silica glass bi-beam samples over a range of humidity values. This work demonstrated how AFM can be used to measure crack tip velocity in a regime where other techniques might not have the necessary resolution to do so.

9. A STATISTICAL MECHANICAL MODEL FOR CRACK GROWTH

9.1. Overview

Crack growth is generally a result of breaking atomic bonds, and bond breaking is both a thermally-activated and mechanically-driven process. A subset of the existing models for cracks have been constructed by a quasi-one-dimensional discrete arrangement of particles along each crack face, where the system is treated mechanically.¹⁵⁷⁻¹⁵⁹ These and other mechanical models have been extended to include thermally-activated rate effects, typically by assuming a simple Arrhenius¹⁶⁰, Eyring¹⁶¹, or Kramers¹⁶² relationship.¹⁶³⁻¹⁷⁰ Critically, it is not clear that treating a crack model system mechanically and combining with an assumed rate law is indeed valid or simply heuristic. Here the original model system is treated using the principles of statistical thermodynamics, rather than the mechanical principle of minimum total potential energy. The thermally-activated, mechanically-driven rate of advancing the crack is obtained in terms of partition functions for the whole system. An analytic relation is then obtained for the crack advancement rate, which is asymptotically valid as the bonded potentials ahead of the crack tip become steep.¹³¹⁻¹³² Under the combined effects of steep potentials and the thermodynamic limit, simplified relations are obtained that closely match past forms of the crack advancement rate. Therefore, in addition to providing generalization, this analysis serves as a necessary validation of existing crack growth relations.

9.2. Summary of Theory and Results

The crack model system consists of a discrete set of particles connected along the crack faces by bending elements and across the crack plane by bond elements. These bond elements only exist ahead of the crack tip. Assuming the crack remains symmetric, the relevant degrees of freedom are the discrete crack face separations q_i and the corresponding momenta $p_i = m\dot{q}_i$ where m is the reduced mass. The Hamiltonian of the system is then

$$H(p, q) = \sum_{i=1}^L \frac{p_i^2}{2m} + U(q) \quad (9-1)$$

where there are M particles ahead of and including the crack tip, N particles behind the crack tip (for a total of $L=M+N$ particles on each crack face), and $U=U_0+U_1$ is the system potential energy. The contribution from bending the crack faces is

$$U_0(q) = \sum_{i=1}^{L-1} \frac{c}{2} (q_{i-1} - 2q_i + q_{i+1})^2 \quad (9-2)$$

where c is the bending element stiffness, and the contribution from stretching bonds is

$$U_1(q) = \sum_{i=N+1}^L u_b [1 - e^{a(q_i-b)}]^2 \quad (9-3)$$

where u_b is the bond energy, b is the equilibrium bond length, and a is the Morse parameter. Treating the system mechanically involves minimizing the Hamiltonian with respect to the degrees of freedom and substituting that solution into mechanical relations for things like force or displacement. Treating the system using statistical thermodynamics involves integration over all possible degrees of freedom in computing partition functions, such as the isometric ensemble partition function

$$Q(N, M, V, T) = \frac{1}{h^L} \int dp \int dq e^{-\beta H(p, q)} \quad (9-4)$$

where V is the fixed position applied at the end of the open crack (displacement controlled), T is the temperature, $\beta=1/k_B T$ is the inverse temperature, k_B is the Boltzmann constant, and h is the Planck constant.¹¹⁸ Computing the momentum portion of the partition function is trivial (integration of a Gaussian function due to the form of the kinetic energy), but the configuration integral

$$Q_{con}(N,M,V,T) = \int dq e^{-\beta U(q)} \quad (9-5)$$

cannot be computed analytically and is difficult to integrate numerically due to high dimensionality. It is required, along with the partition function of the system in its transition state (all configurations with the crack tip bond fixed in its transition state), to compute the rate of breaking the crack tip bond according to transition state theory¹⁷¹

$$k = \sqrt{\frac{1}{2\pi m \beta}} \frac{Q_{con}^\dagger}{Q_{con}} \quad (9-6)$$

A portion of the integrals nested within the configuration integral can be computed analytically, leaving a function within the integrand to be integrated over the remaining degrees of freedom. The degrees of freedom that can be integrated over analytically are all those behind the crack tip; if the crack face separations ahead of and including the crack tip are now written in terms of the bond stretches $\lambda_i = q_i / b$, this would be

$$Q_{con} = \int d\lambda Q_{0,con}(\lambda) e^{-\beta U_1(\lambda)} \quad (9-7)$$

Note that the function $Q_{0,con}(\lambda)$ is the configuration integral of the reference system, i.e. the system with bonds ahead of and including the crack tip fixed at some set of bond stretches. Assuming that these bonds are sufficiently stiff and high in energy compared to available thermal energy, the recently developed asymptotic approach¹³¹⁻¹³² can then be used to analytically approximate the configuration integral of the full system in terms of the analytic-and-exact relation for the reference system and certain corrective factors. This has been accomplished but is not shown here for simplicity (relatively large number of long equations). However, it has been implemented in the Python package `statMechCrack` along with a Monte Carlo method of computing the configuration integrals numerically. Preliminary results when computing the rate of breaking the crack tip bond as a function of load are shown in Figure 9-1.

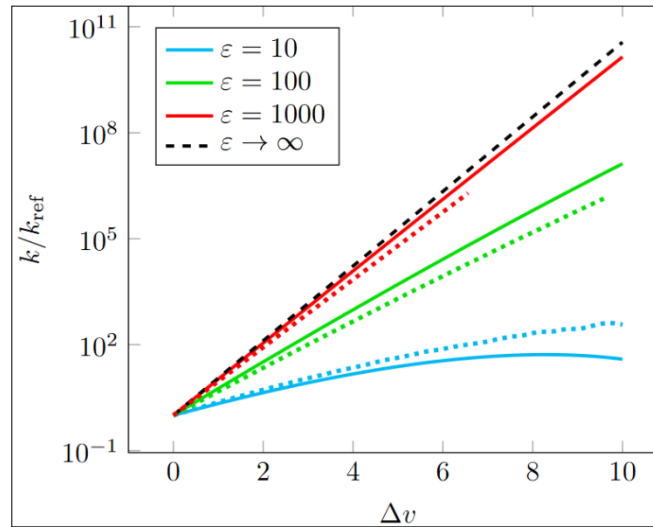


Figure 9-1: Plot of the rate of breaking the crack tip bond as a function of the displacement applied to the crack, relative to the rate at zero displacement, while increasing the scale of the bond energy relative to thermal energy. The asymptotic approach (solid) and the Monte Carlo calculations (dashed) converge as the energy increases, while also approaching the infinite energy limit.

9.3. Conclusion

The principles of statistical thermodynamics were applied to a crack model system that has been previously treated mechanically. This was done in order to arrive at a thermally-activated mechanically-driven relation for the rate of advancing the crack in terms of molecular parameters. An asymptotic approach was applied to the resulting theory in order to obtain analytic relations. Through comparison to Monte Carlo calculations, this approach was verified to become accurate as the strength of bonds ahead of the crack tip became large. Ongoing and future work will involve considering the fixed-force ensemble and determining simplified relations for large systems.

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