THE ROLES OF ATOMIC-SCALE DYNAMICS AND STRUCTURE IN THE BRITTLE FRACTURE OF SILICA

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ABSTRACT

We modeled the initiation of fracture in vitreous silica at various strain rates using molecular dynamics simulations. We avoided biasing the location for fracture initiation within the sample so that we could study the effects of dynamics and structure on determining the path to fracture, defined as the particular bonds that break during the course of fracture. We sought to show that the path to fracture would be primarily determined by the local variations in the structure of the vitreous phase at low strain rates, with diminished sensitivity on structural variations at higher strain rates. However, the results of our model indicate that the path to fracture is dependent not only on the initial structure of the system and the applied strain rate, but also on the initial phase of the thermal vibrations. This underscores the importance of atomic dynamics in determining the path to fracture in brittle materials and provides a justification for extending the analysis of fracture surfaces to the near-atomic scale.

INTRODUCTION

Although brittle fracture is a seemingly familiar process, there is no consensus on the atomistic processes involved. This stems from the fact that brittle fracture is a rapid process, and current analytical techniques are not capable of imaging materials on both the appropriate size and time scales involved. The fractoemission analysis technique of Dickinson et al.¹ is one of the only currently available techniques that can provide dynamic fracture information on the activities of individual atoms and breaking bonds. Although this technique provides important insight into the dynamics of brittle fracture, it cannot provide a comprehensive understanding of the atomic mechanisms involved.

We chose to perform molecular dynamics simulations to elucidate the roles of atomic-scale dynamics and structure during brittle fracture. Molecular dynamics (MD) gives us the ability to see with detail all aspects of a system undergoing fracture. The tricky part of using MD to model fracture is not necessarily performing the simulations, but analyzing the results of the simulations. For example, there is a tendency for people to draw a direct comparison between the stress-strain curves derived from MD simulations with those obtained from experiment. We will explain what the limitations to direct comparison are, and we will show that the simulation of a small system having simple potential functions, with proper analysis, can provide insight into brittle fracture that the simulation of much larger systems, lacking proper analysis, cannot.

METHOD

We performed molecular dynamics simulations on silica-like systems using a two-body interatomic potential function proposed by Soules². The characteristics of the simulated vitreous silica systems resulting from this potential are summarized by Ochoa et al.³ For this study, we used systems containing 1152 atoms with full periodic boundary conditions.

We obtained simulated 300 K vitreous silica structures by quenching a 12,000 K liquid derived from melting a high-cristobalite structure. Both the quench and temperature ramp-up

were performed at a rate of $1 \text{ K} \cdot \text{fs}^{-1}$. Because of limitations in the potential, the absence of free surfaces, and the short simulation time, the melting temperature of this system, 10,000 K, is greatly elevated over the accepted melting temperature of cristobalite, 2090 K.

We simulated fracture by uniaxially straining systems to failure. Because of the small size of our system, we essentially model the small volume of material near a flaw or in front of an advancing crack tip that undergoes significantly greater strain than the macroscopic sample as a whole. Strain was applied by scaling the size of the periodic cell and uniformly scaling the positions of particles within the cell at periodic intervals during the simulation. This method ensures that there is no bias to fracture at any particular location. The range of applicability of this method of strain application extends to strain rates as high as about 0.2 ps^{-1} for samples of the size used here when using arguments based on crack propagation velocities, as shown in Fig. 1. Our simulations find that the fundamental mechanical and fracture behavior of the system changes at this same strain rate, indicating that it is near this strain rate that the processes that limit the rate of brittle crack propagation occur.

Figure 1. Geometric interpretation of maximum strain rates, based on crack propagation velocities, system size, and strain at failure. (a) Initial dimensions. (b) Average 0.08 strain in material outside of crack region, as observed in typical fracture experiments. (c) Additional 0.12 strain added in strain region ahead of crack, equal to strain in controlled-atmosphere experiments. We assume the width of the high strain region to be on the order of our $20 \text{ \AA}$ sample width. A crack propagating through this region at a velocity is 2250 m/s ($0.6 \cdot v_s$ for v -silica) gives a high strain period of 0.889 ps for the final 0.12 strain, a strain rate of 0.135 ps^{-1} . Uncertainties in predicting the size of this high-strain region in a real system suggest the actual value should lie within an order of magnitude of this value. Since the elastic modulus of our system is larger than that of vitreous silica, a maximum strain rate of about 0.2 ps^{-1} is suggested for our system.

We simulated fracture at a range of strain rates and under various conditions to probe the intricacies of brittle fracture. We applied strain rates ranging from 0.005 ps^{-1} to 50 ps^{-1} to examine the gross system response at wide range of strain rates. We then concentrated on strain rates near 0.2 ps^{-1} , ranging from 0.05 ps^{-1} to 0.5 ps^{-1} , to see how the fracture behavior changes in this strain rate region, and examined the effects of structural perturbations on the ultimate path to fracture and the strain rate sensitivity of these effects. The results presented in this study are

mainly stress-strain curves and real-space images of the path to fracture in simulated systems, and our analysis link these results to results from real fracture experiments.

RESULTS

We will focus on three key results of MD fracture simulations. The first is that brittle fracture on the atomic scale looks different than fracture on the macroscopic scale. The second is that the nature of the fracture process is dependent on the strain rate. The third is that the path to fracture is influenced by individual atomic motions.

A distinguishing feature of brittle fracture is that it results in little macroscopic deformation beyond the creation of fracture surfaces. The simplest model of this process is the "unzipping" of atomic bonds between a pair of atomic planes with no associated permanent deformation beyond those atoms. This model may be appropriate for describing the cleavage fracture of single crystals such as ionic salts, but not the fracture of amorphous solids where there are no neatly aligned planes on which this kind of orderly bond breakage can occur. Additionally, it has been observed that even cleavage fracture in single crystal samples will eventually come to an end as cracks advance across large samples, giving way to mist and hackle as seen in materials such as glass⁴. Clearly, we need to rethink this model that is applicable only to very limited conditions.

Our simulations suggest that brittle fracture models of amorphous materials need not constrain bond breakage to only those bonds that would otherwise span the crack, the amorphous equivalent of the bonds between cleavage planes. Macroscopic measures of brittle fracture in these materials do not require that a reconstructing strain be limited to a single layer of atoms in a brittle material, only that it be limited to a small volume as compared to the entire system. We find that structural rearrangements occur throughout the simulated near-crack-tip region sample by the breakage of isolated bonds resulting from inhomogeneous bond environments under high strain. Since there is no long-range ordering of these rearrangements to relieve stress in an extended volume, fracture would still appear to be brittle from a macroscopic standpoint. The energy released as this reconstructed high-strain layer falls back into an unstrained state after fracture may result in the latent fractoemission observed by Dickinson et al.

A comparison of the stress strain curves obtained by simulation to those generated from experimental results is shown in Fig. 2. The simulated systems fracture at about 15-20% strain because they are not large enough to allow for stress-intensity effects. This is comparable to the maximum strains observed before fracture of flaw-free pristine silica fibers in vacuum which are also free of stress-intensity effects. The simulated elastic modulus is higher than that of real silica, resulting in a significantly higher fracture stress in the simulated systems.

We find that brittle fracture in amorphous materials is a strain rate dependent process, in agreement with previous MD simulations by Ochoa and Simmons⁵. Both the maximum stress and the strain at maximum stress increase with strain rate, as shown in Fig. 3. Note that the structure becomes significantly stiffer at strain rates above 0.5 ps^{-1} , approaching a maximum value at 20 ps^{-1} . The increase in both the system stiffness and the overall fracture energy at the strain rate corresponding to the maximum crack propagation velocity indicates that this behavior may be responsible for limiting crack propagation velocities. Marder et al.⁶ point out that although continuum models predict that crack propagation velocities should approach the Rayleigh wave velocities, they in fact rarely exceed 0.4 to 0.6 of this speed. The failure of these continuum models to accurately predict crack propagation velocities may reflect that they only account for the limits in the ability of the propagating crack to make its presence known to the material in its path and do not account for the lattice effects that make fracture more difficult as the local strain rate approaches a limiting value.

Figure 2. Stress-strain curves from simulation and experiment are distinctly different. Simulation curve is for a system strained at 0.05 ps^{-1} , "air" is for a system fractured in air, after Kurkjian⁷, "LN₂" is for a sample fractured in liquid nitrogen, after Proctor⁸. Linear elastic modulus of 72.5 GPa is assumed for fracture strains in experimental systems.

Figure 3. Both the rigidity of the structure (maximum stress) and the strain at maximum stress increase with strain rate. The strain rate here is plotted both in units of ps^{-1} and in terms of a thermal vibrational period.

The initial aim of our fracture simulations was to show that there are structural variations in amorphous structures that determine the path to fracture. We developed a "free volume sphere" method to find largest interstices in these structures, with the expectation that the fracture path would include these voids. However, we found that fracture did not always occur at the largest voids present. We also found that the location of fracture in a structure could be completely different at different strain rates, as is shown in Fig. 4. Our simulations also show that the probabilistic path to fracture becomes more diffuse, and may bifurcate, as the strain rate increases towards its upper limit, as is evidenced by the images of the fracturing systems shown in Figs. 4 & 5. Thus we find that the path to fracture can be influenced by the dynamics driven by the application of strain as well as the structure of the system.

Figure 4. Fracture locations in same system at different strain rates. (a) 0.005 ps^{-1} , (b) 0.1 ps^{-1} .

Our simulations also show that the particular path to fracture is influenced by thermal vibrations and other small perturbations in structure. In order to investigate these effects, we performed a series of simulations at strain rates of 0.05 ps^{-1} and 0.5 ps^{-1} where we fractured the sample after different hold times to probe the effects of the vibrational state of the system, after stopping and re-starting the simulation to perturb all atomic positions by reducing the position

with which they were specified, and after slightly perturbing the position of one atom in the system. This is an expansion of previously reported work by these authors⁹.

Of the three types of perturbations examined, annealing the system for different times before fracture had the largest effect. In this case, the structure is still essentially the same because the system is well below its glass transition temperature. However, thermal vibrations perturb each atom in the structure by about $0.1 \text{ \AA}$, whereas the other perturbation methods perturb atomic positions by at most $10^{-5} \text{ \AA}$. The effects of thermal vibrations on the path to fracture of a sample strained at 0.5 ps^{-1} is illustrated in Fig. 5. Note that the location of fracture occurs in completely different regions of the sample at different times. In general, we find that the effects of this type of perturbation on the particular path to fracture are enhanced at the higher strain rates. The variations of the paths to fracture for samples strained at 0.05 ps^{-1} are significantly less. The effects of perturbations are evident in the stress-strain curves at both strain rates as shown in Fig. 6.

Figure 5. Fracture locations in same system after different anneal times at 0.5 ps^{-1} strain rate. (a) 1 ps, (b) 2 ps.

Figure 6. Variation in stress strain curves for the same systems at different anneal times and strain rates. (a) 0.05 ps^{-1} , (b) 0.5 ps^{-1} .

The other methods of perturbing the structures, round off and single atom perturbation, had a lesser effect on fracture. Both methods resulted in real space images of fracture that were scarcely different, but effects of both could be discerned in stress-strain curves. The effects of round off were greater than the effects of single atom perturbation. Since the effects of both grew over time, these effects were more pronounced at the lower strain rate than at the higher strain rate, because fracture took longer and system behaviors had more time to diverge.

CONCLUSIONS

Computer simulations of brittle fracture currently provide the best means of studying this process on the atomic scale because currently available analytical techniques cannot image fracture at this scale during the event. With some care in the interpretation of results, one can gain important insights into the brittle fracture process, even with simple potentials and systems of limited size.

We find that the fracture behavior of simulated systems changes markedly as strain rates approach those corresponding to maximum crack propagation velocities. As the system is pushed to higher strain rates, the structure becomes more rigid, the fracture path becomes more diffuse, and bifurcation of the fracture path may occur. This provides an explanation for dynamic crack branching during rapid fracture of a brittle material.

We also find that the path to fracture shows extreme sensitivity to all aspects of a dynamic system, from the applied strain rate to the state of thermal vibrations. Although the structure of an amorphous system clearly plays a role in its path to fracture, it is not the sole determining factor of the path to fracture in an otherwise unbiased system. This behavior should not be limited to the fracture of amorphous materials, but may occur in all materials where individual atomic motions can cause a crack to change its path, even those that would otherwise tend to fracture by cleavage.

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REFERENCES

1. J.T. Dickinson, S.C. Langford, L.C. Jensen, G.L. McVay, J.F. Kelso, C.G. Pantano, J. Vac. Sci. Technol. A **6** (3), 1084 (1988).
2. T.F. Soules, J. Non-Cryst Solids **123**, 129 (1990).
3. R. Ochoa, T.P. Swiler, J.H. Simmons, J. Non-Cryst. Solids. **128**, 57 (1991).
4. Y.L. Tsai, J.J. Mecholsky, Jr., J. Mater. Res. **6**, 1248 (1991).
5. R. Ochoa, J.H. Simmons, J Non-Cryst Solids **75**, 413 (1985).
6. M. Marder, S Gross, J. Mech. Phys. Solids **43**, 1 (1995).
7. C.R. Kurkjian, U.C. Paek, Appl. Phys. Lett. **42** (3), 251 (1983).
8. B.A. Proctor, Physics and Chemistry of Glasses **31** (2) 78 (1990).
9. T.P. Swiler, T. Varghese, J.H. Simmons, J. Non-Cryst. Solids **181**, 238 (1995).

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