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Deformation and Fracture of a SiO_2 Nanorod

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The failure response to uniaxial tension and compression of a nanorod of SiO_2, in the form of a stack of six-membered rings (Si_6O_{18}) with appropriate termination at the two ends, is investigated at the molecular level. A 144-atom rod is shown to exhibit meaningful mechanical instability that can be compared with simulations of bulk quartz; at the same time it is small enough for the interatomic forces to be treated quantum mechanically. The present work is a prelude to the study of the effects of water on the mechanical strength of silica, a fundamental issue in understanding the dislocation mechanisms of hydrolytic weakening.

Keywords: Nanorod; Silica; Failure; Hydrolytic weakening

INTRODUCTION

Understanding the strength of material is a problem of longstanding interest, for reasons of fundamental science as much as for practical applications [1]. From a theoretical standpoint one can imagine the maximum resistance of a material to deformation can be determined by regarding the material as an assembly of interacting atoms, the cohesive or binding energy of which is known for arbitrary interatomic separations, the strength then being specified by an inflexion point in the variation of this energy with deformation (strain). In principle, this approach applies to a small cluster of atoms as well as a bulk crystal. Current interest in nanoscience and technology has stimulated an awareness that mechanical behavior in small dimensions can have significant deviations from properties normally associated with structures at the two extremes, an isolated cluster of atoms or a macroscopic specimen. Unlike physical properties which deviate from continuum behavior only on the atomic scale, mechanical strength and deformation are controlled by defects in the assembly which in themselves can range from angstrom to nanometer to micrometer length scales [2].

As a material system with properties of interest on different length scales, SiO_2 has particular appeal to more than one scientific community, given its importance in electronic and optical applications, and its considerable significance as a material in geosciences. In this work, we are motivated to study SiO_2 at the nanostructure level, distinct from small clusters and bulk crystals. We introduce a nanorod as a novel, stand-alone system which has advantages over a cluster in that meaningful mechanical behavior can be extracted and scaled up continuously to larger dimensions. The rod is also more suitable than a bulk system for the study of the effects of stress and chemical reaction because one has better control over the atomic site for structural defect nucleation or chemical bond reaction.

The study of mechanical behavior of the nanorod entails the proper description of interatomic interactions. Empirical potentials developed from fitting physical properties are available in the literature; a number of these models have been found to give reasonable predictions. A problem, which all empirical potentials have, is to treat correctly the effects of charge transfer when interatomic bonds are broken or formed. We are adopting the approach of using the available empirical potentials while also testing their consistency and robustness in the context of the mechanical behavior of the nanorod. At the same time we are developing quantum

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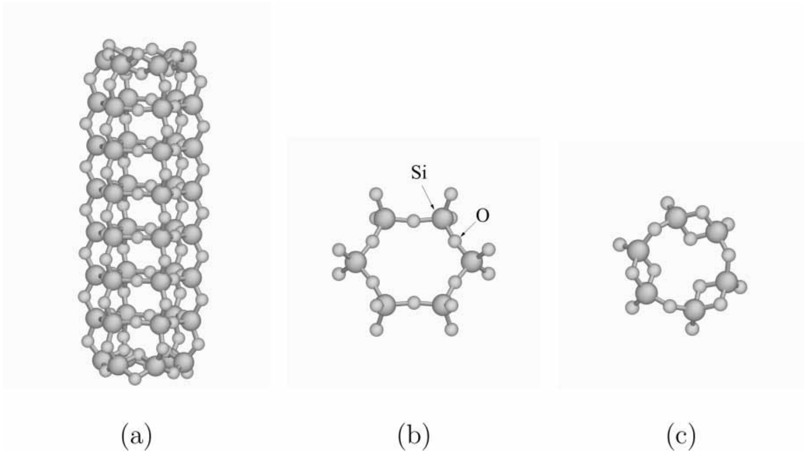

(a) (b) (c)

FIGURE 1 Structure of (a) a relaxed nanorod, (b) an interior ring, (c) an end ring.

mechanical methods for treating the interatomic forces, and will apply them not only to the nanorod, but also to the effects of water on the strength and deformation of the nanorod.

In what follows we will describe the structural characteristics of the nanorod and present a molecular dynamics study of uniaxial tension and compression, where the nanorod results are also compared with the bulk simulations. This is followed by a discussion of extending the present work to clarify the effects of water on the strength of the nanorod, in the context of the phenomenon of hydrolytic weakening in quartz. The paper concludes with several remarks on work in progress.

NANOROD CONSTRUCTION

A nanorod composed of 144 atoms (48 SiO_2 molecules) is shown in Fig. 1(a). Our construction of a nanorod first involves the formation of hexagonal planar six-membered rings, Si_6O_{18}. As shown in Fig. 1(b), each Si_6O_{18} ring contains six corner-linked SiO_4 tetrahedra, where each tetrahedron has two bridging oxygen atoms that are shared with two neighboring tetrahedra. It can be seen from Fig. 1(b) that, for each Si_6O_{18} ring, there are six Si atoms and six O atoms lying within the plane of the ring, and six O atoms each above and below the plane, respectively. Then, the nanorod is assembled by stacking such rings (layers) one over another. Each interior ring is linked to two adjacent rings by sharing O atoms. For the structure to be free from dangling bonds, the nanorod is capped at the ends by "terminating" rings in which the six Si atoms are connected alternately by a bridging oxygen or two oxygens, in the manner shown in Fig. 1(c). Each end layer has 21 atoms, whereas each interior layer has 24 atoms; an eight-layer rod, therefore, has a total of 144 atoms. The ratio of Si to O atoms in a nanorod is exactly 1:2, leading to a stoichiometric silica nanorod. Though the nanorod is an idealized structure created to facilitate the study of water interaction with strained Si–O bond, similar crystal structure occurs in nature, for example, in cyclosilicate mineral beryl $Be_3Al_2Si_6O_{18}$ six-membered ring Si_6O_{18} are linked to Be^{2+} and Al^{3+} ions.

We have verified the stability of our idealized structure by performing energy minimization calculations using two sets of interatomic potentials for SiO_2, developed by Tsuneyuki *et al.* (TTAM) [3] and by van Beest *et al.* (BKS) [4]. Both potentials are expressed as the sum of a short-range interaction of the (exp-6) form and a Coulomb interaction with fixed charges. The initial Si–O bond length was taken to be the optimized value for bulk α-quartz given by the model potential, $d_{SiO} = 1.63$ Å. Thus, $d_{OO} = 2.66$ Å and the nominal length of the eight-layer nanorod is $8d_{OO} = 21.28$ Å. Relaxed bond distances and bond angles obtained are given in Table I, along with experimental measurements and values obtained by relaxation of bulk α-quartz lattice. Two values are given for each type of bond angle, referring to inter- and intra-ring bond angles, O–Si–O or Si–O–Si, respectively. It can be seen that the geometry of the relaxed nanorod using TTAM is very close to that for BKS.

TABLE I Structural parameters for the bulk quartz and relaxed nanorod

	Exp	*TTAM-bulk*	*BKS-bulk*	*TTAM-rod*	*BKS-rod*
d_{Si-O} (Å)	1.61	1.63	1.63	1.66	1.62
θ_{O-Si-O} (°)	109.4		109.5	126.1,109.7	124.8, 109.5
$\theta_{Si-O-Si}$ (°)	143.7	147	148	126.7, 177.4	125.5, 175.9

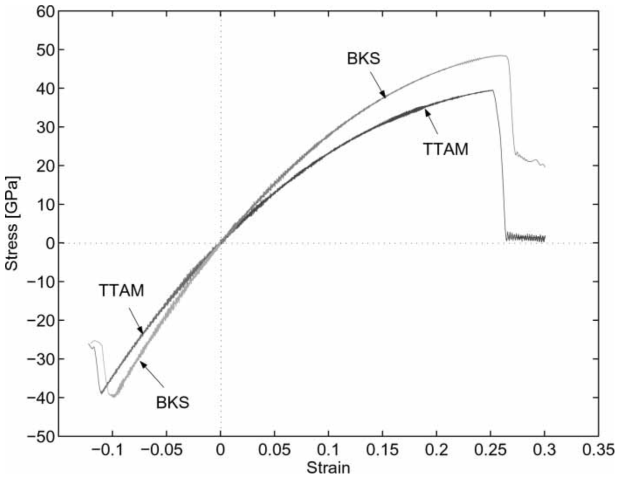

FIGURE 2 Stress vs. strain curves for uniaxial tension and compression of a nanorod.

The inter-ring bond angles of Si–O–Si and O–Si–O are approximately the same, while the bond angles of Si–O–Si and O–Si–O in the plane of the ring are different. The parametrizations of TTAM and BKS have been tested recently via the nanorod using high-level *ab initio* electronic structure data [5].

DEFORMATION AND FRACTURE OF NANOROD

Uniaxial tension and compression of a stand-alone nanorod are performed by molecular dynamics (MD) simulations in which the Coulomb interactions between each pair of atoms are evaluated directly. System temperature is maintained at 1 K by velocity rescaling. Deformation is initiated by using the 32 atoms in each end layer as grips, with each atom given a prescribed velocity in the loading direction, and all atoms in the rod are allowed to relax. To characterize the stress state of the nanorod we take the sum of all forces acting on the cross section divided by the initial cross section area $A_0 = 4\pi d_{\mathrm{OO}}^2 = 88.9\,\text{Å}^2$. For the measurement of strain we take the elongation of the rod divided by the initial gage length (distance between two grips) $l_0 = 13.3\,\text{Å}$.

The stress–strain curves thus obtained for uniaxial tension and compression are shown in Fig. 2. It can be seen that the nanorod deforms linearly in the early stages, then the stress–strain variation becomes nonlinear up to the point of failure where the stress changes precipitously. Values of the critical stresses and strains at the onset of structural failure are listed in Table II. The tensile strength obtained for BKS is somewhat greater than that for TTAM, with very similar corresponding critical strains. In compression the two potentials give about the same strength and critical strains. Comparing the nanorod responses with those of crystalline SiO$_2$ obtained using BKS [6], we see similar results in tension but very different results in compression.

We show in Fig. 3(a), (b) the atomistic details, obtained for TTAM, when the nanorod fails in uniaxial tension and in compression. In tension the in-stability occurs by bond breaking between the rings, showing that the tensile strength is governed by the cohesive limit of Si–O bonds, an intrinsic material property. Thus the stand-alone rod and bulk SiO$_2$ can be expected to have similar tensile strength, one that is insensitive to size or geometric effects. In contrast, under compression the rod is seen to fail in a buckle manner. It is known from macroscopic analysis of buckling of columns that the critical load depends on the length and cross section area of the column. We therefore, expect our nanorod results to have significant system size effects. In previous simulations of compressive failure of carbon nanotubes with different ratios of length L to diameter D, we have indeed observed different critical load variations with the L/D ratio, from a load that is insensitive to L/D at small ratios to a loading varying as the reciprocal of L/D at large ratios [7]. Additionally, we also know that the instability in bulk SiO$_2$ under uniaxial compression occurs as a crystal-to-amorphous transition, at the much lower threshold of 14 GPa [8]. Taken together, our results show that the deformation behavior of the nanorod will be different from that of the bulk in compression, but not in tension.

To investigate the effects of temperature on deformation and fracture, we repeat the uniaxial tension simulation, previously performed at essentially zero temperature (1 K) now at 100 K. Instead of the homogeneous process of bond breaking between two adjacent rings (layers) in a cleavage manner, we observe a localized mode of bond breaking and subsequent rebonding. Two snapshots right before

TABLE II Failure stresses and strains

		Critical stress (GPa)		*Critical strain*	
		TTAM	*BKS*	*TTAM*	*BKS*
Tension	Nanorod	39.6	48.4	0.262	0.266
	Bulk		41.5		0.25
Compression	Nanorod	− 38.6	− 39.6	− 0.11	− 0.098
	Bulk		− 14		− 0.12

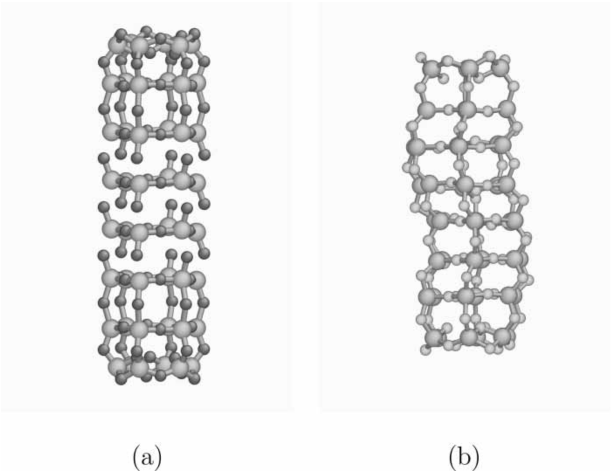

FIGURE 3 Failure pattern by TTAM potential at 1 K: (a) tension, (b) compression.

and after fracture are shown in Fig. 4(a), (b). As the rod approaches a point of prior to rupture, it assumes an atomic configuration, where the two parts undergoing separation is held together by a single chain of atoms. In the "saddle-point" configuration, clearly seen in Fig. 4(a), we have an example of strain localization on the single-atom scale, the chain being the "neck" in the tensile test specimen. When rupture does occur, rebonding takes place at the two newly formed ends, as can be readily discerned in the lower half of the fractured rod in Fig. 4(b). Comparing this to the response at 1 K, it is clear that thermal activation is responsible for the change from a clearly brittle fracture to a much more ductile rupture.

We believe the single-chain rupture mode just described could be a general feature of how nanostructures respond under tensile strain to failure. Similar behavior has been seen by Rodrigues and Ugarte [9] experimentally in the elongation of a Au nanojunction, one atom thick, by *in situ*, real time re-solved high-resolution transmission electron microscopy. Molecular dynamics simulation of the rupture of a Au nanowire, a system of about 70 atoms, also has been reported by da Silva *et al.* [10]. The simulation showed that under tensile loading the central atoms in the cylindrical wire displaced toward the surface such that a seven-atom plane transforms into a six-atom ring (cf. our nanorod structure), the atoms evolving to a configuration of a single chain of three or four atoms. Detailed results of the bond lengths in the chain, experimentally observed and simulated, show impressive correspondence. We interpret these results, as well as our own, to signify a process of strain localization prior to single-chain rupture which occurs in a cooperative manner. In future studies of nanostructure deformation it would be of interest to see whether this failure mode has any generality.

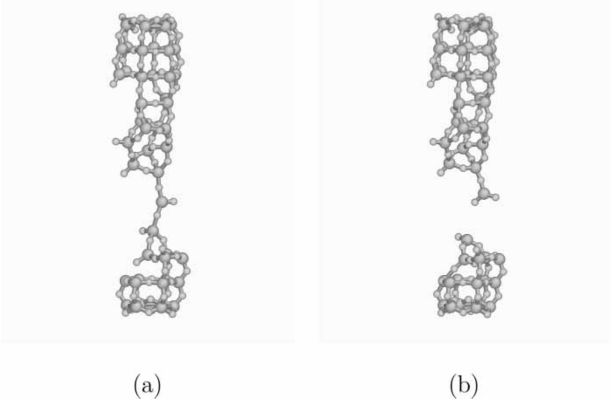

FIGURE 4 Failure pattern at 100 K (a) before failure, (b) after failure.

TOWARDS UNDERSTANDING HYDROLYTIC WEAKENING OF QUARTZ

Our interest in the SiO_2 nanorod has another motivation, that of probing the effects of water on the strength of SiO_2. In 1965, Griggs and Blacic [11] reported the anomalous weakness of synthetic quartz at high temperature, a phenomenon which has come to be known as hydrolytic weakening. Basically the observation was that while at temperature of 300°C synthetic quartz specimens have high compressive strength (2 GPa) similar to natural quartz, at elevated temperatures, 400–600°C the strength dropped rapidly as the specimens underwent large plastic deformation without fracture. The interpretation given was that the synthetic crystals contained water which hydrolyzed the silicon–oxygen bonds, forming SiOH silanol groups which became mobile to promote dislocation mobility [12]. This problem has been actively investigated in the ensuing years [13,14], including molecular calculations at the empirical potential [15,16] and *ab initio* [17–19] levels. It is fair to say that at present the issue of the dominant mechanism for the observed plasticity is still unresolved. The controversy, stated in an overly simplified way, lies in deciding which of the two competing candidates, dislocation nucleation versus dislocation mobility, as being responsible for the increased dislocation activity seen at elevated temperatures.

Our goal is to approach this problem from the combined perspective of quantum chemistry and mechanics of deformation, in the hope of contributing to the clarification of a more limited issue, the role of the interaction of H_2O with SiO_2 on strength. Using the nanorod as the specimen of interest we are in the process of studying the deformation and failure behavior when one or more water molecules is introduced and chemical reactions are allowed to take place. We are using classical empirical potentials which have been used to study the effects of water on the surface and stability of quartz by de Leeuw *et al.* [20], as well as molecular orbital methods.

In addition, we are applying the method of transfer Hamiltonian, based on the parametrization of a semi-empirical Hamiltonian in the neglect of diatomic differential overlap (NDDO) approximation [21]. An important issue, already present in the study of the SiO_2 nanorod, is the effect of charge transfer when bonds are broken or formed. The question becomes even more critical when water molecules are introduced into the system. In view of the inability of classical potentials to model properly charge transfer effects, quantum mechanical treatment is inevitable. While quantum chemical and density function theory methods are available, the methods are not equally accurate with regard to electron correlation or computationally tractable with regard to dealing with a large number of atoms. In this respect the advantages of the transfer Hamiltonian method are first it retains the accuracy of *ab initio* quantum chemistry at the level of coupled-cluster theory, a high-level method for electron correlation [22]. Secondly, because it involves informed parametrization the method is several orders of magnitude less computationally demanding than coupled-cluster calculations. We show in Fig. 5a comparison of the stress–strain response of the SiO_2 nanorod obtained using the transfer Hamiltonian method with those for BKS and TTAM. For this comparison, the nanorod is loaded at a higher strain rate compared to the quasi-static limit shown in Fig. 2 considering that the calculation using the transfer Hamiltonian method is still relatively slow. The quantum mechanical forces are seen to result in higher tensile strength and smaller critical strain than the classical simulations; overall the quantum description seems to give a more rigid system.

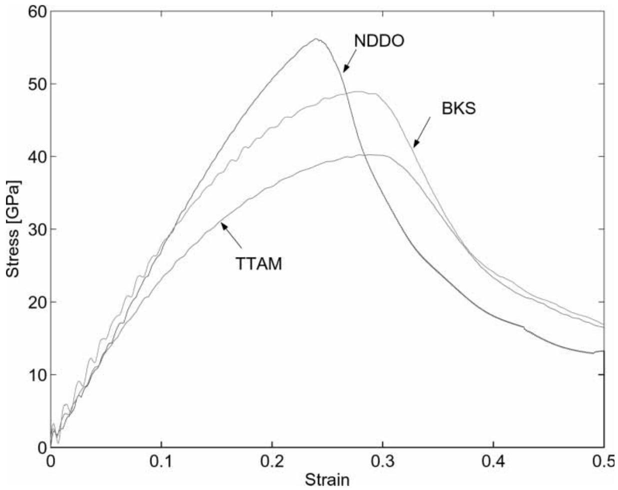

FIGURE 5 Stress–strain curves for uniaxial tension of nanorod using the transfer Hamiltonian method, BKS and TTAM.

DISCUSSION

We have proposed a nanorod for the study of atomistic processes and mechanical behavior in structures that are neither cluster-like nor bulk. The rod is a stand-alone cylindrical assembly of a hundred or so atoms which retain the characteristic structural unit of quartz; its geometric features can be readily scaled up to those of a wire, tube, or even column, yet at the same time it is small enough that full atomistic or electronic structure calculations can be performed. We have shown that the mechanical behavior of the nanorod can be meaningful compared to bulk deformation results, while there are also interesting differences such as deformation under compression. Given the current interest in mechanical stability as well as electronic properties of nanoscale materials [23] we feel that understanding the mechanical behavior of the nanorod at the molecular level will be of interest in nanoscience and technology. Now that silica nanowires, with 5–100 nm diameters, have been recently synthesized by Pan *et al.* [24], one might look forward to the prospect of having actual specimens on which mechanical deformations can be performed.

Our interest in the nanorod extends to probing the effects of water on nanostructures where one can focus on a particular site for the chemical reaction. The nanorod provides a particularly convenient structure in this respect in that in addition to allowing the water molecule to interact with any exposed surface of the rod, we can designate a special location by creating a notch in the rod. This surface defect, by virtue of the strained bonds, then acts as a catalyst for the chemical attack in the same way that it provides a nucleation site for mechanical deformation under stress. We have already demonstrated the utility of a rod with single and double (symmetric) notches with regard to deformation studies. We expect similar benefits in probing the local-environment effects when Si–O–Si is hydrolyzed by H_2O. Probing the interaction of H_2O with SiO_2 is a central theme in a collaborative project of which our work is a part and which includes other investigations of water–silica interaction [25]. In view of the complexity associated with resolving the dislocation nucleation versus mobility issue, we will focus on probing how water reacts with the nanorod individually and collectively.

The application of the transfer Hamiltonian method to the nanorod is expected to give a quantitative measure of the importance of developing a materials modeling approach that is truly predictive. The hope is that this will provide a means to perform MD simulation while retaining the predictive capability of coupled cluster theory. In this spirit we have developed and validated an acceleration scheme for MD simulation using an empirical potential and the transfer Hamiltonian method, the latter being computationally intensive and therefore applied only intermittently. We hope to report on those studies in a future publication.

Acknowledgements

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