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Molecular dynamics simulations of nanoporous organosilicate glasses using Reactive Force Field (ReaxFF)

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ABSTRACT

The structure and properties of nanoporous organosilicate glass (OSG) structure models with 30–70% porosities and different pore morphologies were simulated using molecular dynamics simulations with Reactive Force Field (ReaxFF) potential. The OSG structures were created from nanoporous silica structures generated using classical molecular dynamics (MD) simulations with partial charge pairwise potentials and a subsequent step of adding hydroxide and methyl groups to the dangling bonds and coordination defects. The nanoporous OSG systems were then fully relaxed using molecular dynamics simulations with ReaxFF and detailed structure analysis performed and properties calculated. Analysis of the OSG systems indicated that the structural features (bond distances and angles) as well as the Q_n distribution of the nanoporous silica backbone structure are consistent with the features of dense silica and that the geometry of the added methyl groups is experimentally accurate, even after ReaxFF relaxation. The elastic modulus of the nanoporous silica was calculated and found to be 24–31 GPa for system with 30% porosity and 0.5–2.5 GPa for those with 70% porosity, consistent with previously reported experimental results.

1. Introduction

Porous silica is of significant interest due to the variability and tunability of its pore structures ranging from the molecular to the nanometer and the micrometer scale, which enables their applications in sensors, catalysis, hydrogen storage, drug delivery, thermal insulation, microelectronics, and photonics [1–3]. Organosilicate glasses (OSG) are nanoporous silica systems that are functionalized by introducing organic content including methyl groups and hydrocarbon chains which, together with the porosity, significantly lowers the dielectric content from 3.9 (amorphous silica) to 2.2–2.8 (OSG) and finds applications as low-k dielectrics in VLSIC (Very Large Scale Integrated Circuit) microelectronic devices [4]. The variability of nanoporous silica and OSG systems (order/disordered structures, large/small pores, high/low organic content, and pore morphologies) makes them well suited to a wide range of applications but there is a lack of reliable information concerning their structure–property relationships.

As a result, atomistic simulations have been applied to understand their microstructures and its relationship to mechanical and other properties. The understanding of OSG is especially limited due to their complex organic–inorganic hybrid bonding and different pore morphologies. This paper addresses these challenges by combining molecular dynamics (MD) simulation protocols to create nanoporous silica structures using MD with ReaxFF relaxation to generate realistic OSG structure models.

The complexity of OSG systems (which is further compounded by the randomized porosity) can make them difficult to characterize by computational or experimental methods. For dense silica experimental methods including NMR (nuclear magnetic resonance) and electron diffraction have been effective in providing some insight into the coordination environments, bond lengths, and bond angles [5]. The addition of light organic elements to the nanoporous silica to form OSG generates an increasingly complex system which has undergone limited experimental analysis, with the expectation of FTIR which has provide information on various bond concentrations [6,7].

Attempts have been made to standardize the description of porosity through the analysis of the fractal geometry, absorption isotherms, and relative elastic modulus (E/E_o) and porosity (P) relationships of the systems [8–11]. Due to the ease of calculating the elastic modulus of experimental and computational systems the relationship between the pore structure and the elastic modulus has been extensively studied by Jain et al., Roberts et al., and Rice, among others, who have demonstrated that it is possible to describe the type of porosity depending on the E/E_o v. P trend [12–14]. Porosity is usually described by fitting the E/E_o v. P relationship with either a power or an exponential fit, through which the value of the coefficient is analyzed [12–14].

Development of nanoporous silica models, used as the basis for OSG structure generation, have focused on creating well-ordered porosity (such as perfect spherical pores) which have not fully captured the variability of experimental porosity [15–18]. Two exceptions include work by Roberts and Garboczi using the finite element method (FEM) and Rimsza and Du using classical MD to investigate the role of different

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porosity regimes on changes in the mechanical properties of nanoporous silica systems [13,19]. Investigation of porosity regimes resulted in the description of randomized porosity as "stacked spherical particles" or "stacked spherical pores" which provides insight into the base structure of the porosity [13,19].

Development of realistic OSG structure models has been met with several hurdles related to the complex structure of the systems. The first is the amorphous nature of nanoporous silica backbone, followed by the randomization of the porosity, and finally the existence of organic groups. The amorphous backbone structure indicates that it is desirable to create large simulations (several thousand atoms) so that statistical analysis of the systems can take place. The size of the system limits the application of more computationally accurate but expensive calculation methods to OSG development including density functional theory (DFT) based methods. While several classical MD force fields have been developed to create computational silica models (including those by Van Beest, Kramer, and Santen (BKS), Hassanali and Singer, Muralidharan and colleagues, and Feuston and Garofalini) none of these take into account the existence of either porosity or organic groups [20–23]. Therefore, it is necessary to implement a multistep approach to create the OSG computational structure models for further analysis.

Another difficulty of atomistic simulations of OSG is the organic–inorganic hybrid nature of the system which generates complex and varied bonding states in the system. The mixed bonding character of these systems pose significant challenges of force fields for atomistic simulations of these materials. More accurate first principles methods, such as DFT, can be employed but they significantly limiting the system size that can be studied due to high computational cost [24]. The recent development of Reactive Force Field (ReaxFF) enabled the description of these complex systems with high fidelity. A previous study of the reaction between poly-dimethylsiloxane (–O–Si $(CH_3)_2$–) and H_2O/SiO_2 demonstrates that ReaxFF can produce the thermal properties and time evolution of products at various temperatures and pressures realistically [25]. The successful application of ReaxFF to this combined silica and hydrocarbon systems clearly demonstrates the advantages of using ReaxFF for complex systems with mixed bonding states.

In this paper a series of OSG structure models were created by combining charge scaling and lattice expansion MD simulations with effective partial charge potentials to generate nanoporous amorphous silica with subsequent addition of organic methyl groups and eventual full relaxation of the structures using MD with ReaxFF. ReaxFF allows for the development of large scale structure models which include the randomized porosity and organic content critical to the microstructure of nanoporous silica and OSG while still generating experimentally accurate structures.

The article is arranged as follows: first a description of the classical MD and ReaxFF methods used in this work, then the development of the initial nanoporous silica models from two different classical MD protocols, the generation of OSG structure models, analysis of the atomic structure and the mechanical properties, followed by discussions and conclusions.

2. Methods and simulation details

2.1. MD simulation procedure

In this work the initial 3000 atom model nanoporous silica systems were developed using the parallel MD simulation package DL_POLY 2.2 with cubic periodic boundary conditions [26]. A set of partial charge pairwise potentials were used which included a long-range columbic interaction with a short-range interaction in the Buckingham form which has been successfully applied to silicate glass simulations by Du and Cormack [27,28]. Berendsen thermostats and barostats were used to control the temperatures and pressure in the canonical (NVT) and isothermal-isobaric (NPT) ensembles used to create the randomized porosity in the simulations. Additional details concerning the classical MD simulations methods can be found in reference [19]. All simulations were performed on the Talon and Eagle supercomputing clusters at the University of North Texas.

2.2. Reactive Force Field (ReaxFF)

ReaxFF, developed by Adri van Duin and coworkers, is a force field based on atomic bond order which allows for the computation of bond formation and disassociation, as well as the modeling of chemical reactions [29,30]. The ability to describe bond formation and bond dissociation arises from the relationship between bond distance and bond order/energy which ReaxFF employs. The calculation scheme of geometry-dependent charge (EEM scheme) is applied to calculate the atomic charges in the computational systems [31]. In ReaxFF the energy of the system is calculated through the use of nine different energy terms in order to consider the various types of interatomic interactions which can occur [29,30]. The equation for the energy of the system is included below [29,30]:

$$E_{sys} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWaals} + E_{Coulomb}.$$

E_{bond} is the energy which is generated from the atom bonding state [29]. E_{over} is an energy penalty for over-coordination of the atom [29]. E_{under} is an energy contribution from the π-electron when it is unbonded [29]. E_{val} is a valence angle term which approaches zero as bond disassociation occurs, ensuring that there is not a sharp transition during bond breakage and formation [29]. E_{pen} is an energy penalty which is included to account for the possible occurrence of stable systems with two double bonds [29]. E_{tors} ensures that the energy dependence torsion angle smoothly approaches zero during bond disassociation [29]. E_{conj} accounts for conjugate effects in the molecular energy [29]. $E_{vdWaals}$ is a long range valence interaction which is accounted for on all atoms and uses a distance corrected Morse potential [29]. Finally, $E_{Coulomb}$ is a columbic interaction which is applied to all atomic pairs [29]. ReaxFF is particularly well equipped to account for bond breakage and formation in complex systems which are too large to be treated with DFT methods due to the focus on maintaining a gradual decrease in the bond energy as atoms move apart, rather than experiencing a stepwise energetic change at a set energy boundary. For further descriptions and functional forms of the nine energy terms which are described above the reader is directed to the original paper in references [29,30].

2.3. Nanoporous silica structure generation: lattice expansion (LE) and charge scaling (CS) methods

Numerous methods of generating nanoporous silica computational models have been proposed in literature including the random removal of silica tetrahedron from dense silica models, the generation of perfectly stacked spherical pores, and randomized mixtures of two phases models with the removal of a sacrificial phase [13,16,17,32–35].

In this work two methods of generating randomized pore structure were used to mimic the complex experimental structures of sol–gel and CVD (chemical vapor deposition) derived nanoporous silica by implementation of the lattice expansion and charge scaling methods, respectively [19,36–38]. The lattice expansion (LE) method mimics a CVD derived experimental nanoporous silica structure and was described by Kieffer and Angell and further developed by Nakano et al. [37,38]. The LE method begins with dense amorphous silica systems produced from a melt and quench method described in pervious papers [27]. After the perfect silica structure has been generated the system undergoes a stepwise linear expansion in all three dimensions by 20%. The 20% expansion results in all the bonds stretching to create a loosely-debonded structure. The expansion step was followed by annealing using classical NVT (constant number of atoms, volume and temperature) MD simulations for 30 ps at 300 K which allows