

## Applications of Atomistic Simulation to Radioactive and Hazardous Waste Glass Formulation Development

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# APPLICATIONS OF ATOMISTIC SIMULATION TO RADIOACTIVE AND HAZARDOUS WASTE GLASS FORMULATION DEVELOPMENT

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## ABSTRACT

Glass formulation development depends on an understanding of the effects of glass composition on its processibility and product quality. Such compositional effects on properties in turn depend on the microscopic structure of the glass. Historically, compositional effects on macroscopic properties have been explored empirically, e.g., by measuring viscosity at various glass compositions. The relationship of composition to structure has been studied by microstructural experimental methods (nuclear magnetic resonance, x-ray spectroscopy, etc.). More recently, computer simulation has proved a fruitful complement to these more traditional methods of study. By simulating atomic interaction over a period of time using the molecular dynamics method, a direct picture of the glass structure and dynamics is obtained which can verify existing concepts as well as permit "measurement" of quantities inaccessible to experiment.

Atomistic simulation can be of particular benefit in the development of waste glasses. As vitrification is being considered for an increasing variety of waste streams, process and product models are needed to formulate compositions for an extremely wide variety of elemental species and composition ranges. The demand for process and product models which can predict over such a diverse composition space requires mechanistic understanding of glass behavior; atomistic simulation is ideally suited for providing this understanding. Moreover, while simulation cannot completely eliminate the need for treatability studies, it can play a role in minimizing the experimentation on (and therefore contact handling of) such materials.

This paper briefly reviews the molecular dynamics method, which is the primary atomistic simulation tool for studying glass structure. We then summarize the current state of glass simulation, emphasizing areas of importance for waste glass process/product modeling.

At SRS, glass process and product models have been formulated in terms of glass structural concepts [1]. These models are now being extended for application to both low-level mixed waste glass formulation [2] and to high-purity actinide stream immobilization [3]. Atomistic simulation is providing input for the development of the process and product models for these new applications. Recent results are described in this paper.

## INTRODUCTION

"Atomistic simulation" refers to a variety of computational techniques for determining structural and dynamic properties of materials. The most powerful of these, through its ability to provide dynamic as well as structural data, is the molecular dynamics method. Through this calculational process, the positions and velocities of all particles are calculated for a succession of timesteps, thus defining the atomic structure and dynamics of the material. Through graphical representation of the calculational results, the glass network can be viewed "directly" as well as being analyzed statistically.

The visualization capabilities of the method alone provide valuable insight into the behavior of glass; the human eye is still the best computational tool for "discerning the presence of collective motions" [4]. However, the wealth of properties which can be calculated from

simulation can be correlated to macroscopic behavior as well, providing direct input to models suitable for process control.

## MOLECULAR DYNAMICS SIMULATION METHODS

In the molecular dynamics simulation technique, Newton's equations of motion are solved for each of a collection of particles (atoms, ions, or molecules) as it interacts with all others. The numerical solution of Newton's equations is straightforward; thus, the key to solving this problem is the specification of the forces between the particles or, equivalently, the interatomic potential function between the particles. Time averages of various quantities and their variances can be related to macroscopic thermodynamic quantities such as pressure, heat capacity, enthalpy, etc., through well-known statistical mechanical developments [5].

Simulations are most commonly done holding fixed the volume of the simulation sample, the number of atoms, and the total energy (the "microcanonical ensemble" of statistical mechanics). Periodic boundary conditions are used to hold the number of atoms fixed and to eliminate surface effects in simulation of bulk materials. Computer technology limits the size of the simulated sample and the simulation time interval; most current published work is based on no more than about 1000 atoms, simulated over periods of the order of nanoseconds.

Many quantities of interest in glass processing, such as viscosity and chemical durability, have been modeled as functions of atomic phenomena such as bond length, bond strength, non-bridging oxygen content, etc. Atomic simulation provides a means of "observing" such phenomena directly, thus providing input to models couched in such terms. The positions of the particles at any given time can also be represented graphically (see Figure 1), thus providing a powerful aid to conceptualizing the structure of a glass.

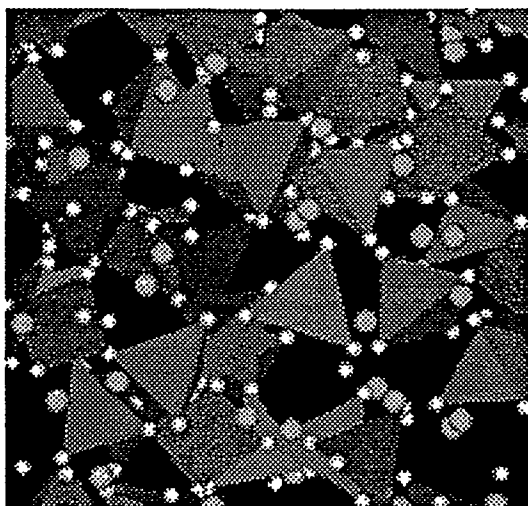


Figure 1. Simulated structure of  $0.50\text{CaO}\cdot 0.50\text{SiO}_2$  glass melt ( $\text{SiO}_4^{4-}$  network units represented as tetrahedra; small circles: non-bridging oxygens; large circles: calcium ions)

The veracity of the simulation must be checked by comparison to microstructural experimental data. Once this is done, simulation can be used to obtain additional quantities which can be obtained by experiment (sometimes with far more difficulty), as well as quantities for which no experimental technique has been developed. An example of the latter is the pair distribution functions, i.e., the radial distribution of atoms of type  $j$  around

an atom of type *i*. These functions describe the environment of an atom in terms of each of the other types of atoms in the system. Experimentally, only the total radial distribution function can be obtained, i.e., the sum of all of the individual pair distributions. The simulation results therefore show how to correctly deconvolute the experimental quantity to reveal the details of the local environments of each atom type.

Other quantities which can be calculated from the simulation results include:

- Sizes, energies, and distribution of "holes" in the glass network. These quantities are related to macroscopic quantities such as electrical conductivity, gas solubility, and activation energies. Significant progress has been made on the well-known mixed-alkali problem in glass science using atomistic simulation [6].
- Non-bridging oxygen (NBO) characterization. This includes the fraction of oxygens which are non-bridging, and the  $Q_n$  distribution, where  $Q_n$  denotes the fraction of silicon atoms (in a silicate glass) having *n* bridging oxygen atoms (i.e.,  $Q_4$  denotes the fraction of completely-polymerized silicon tetrahedra,  $Q_0$  the fraction which are completely isolated from the network). These quantities have been related to macroscopic parameters such as viscosity [1].
- Ring statistics. These characterize medium-range order in the glass [7]. The presence of rings larger or smaller than the optimum for that network (e.g., six-membered rings for pure silica crystal) represents "defects" in the structure which have been used to characterize viscosity [8] and diffusion [9].

## ATOMISTIC SIMULATION OF GLASS

At present, most of the simulation work which has been performed is on bulk glasses of one or a few components. The primary attention has been applied to silicate glasses, although studies of phosphate glasses [10] and borates [11] have also been performed. Numerous studies have been made of vitreous silica [12-14], whose properties have been well-characterized experimentally and whose behavior, which is in several respects atypical of oxides, provides a rather stringent test of interatomic potential functions. Thus, the focus of many of these studies is on developing and verifying a proposed interatomic potential function. Potential functions which model silica glass structure well provide a good basis for extension to multicomponent silicate glass systems.

Oxide structure is uniquely determined by its mixed covalent-ionic character. Locally, the bonds are directional, a reflection of the covalent nature of the constituents. In this way the oxides are similar to very covalent materials like silicon. On the other hand, the bonding is also ionic, leading to long-range electrostatic interactions which are similar to the case of materials like NaCl. These aspects are interdependent. The available interatomic potentials which appear most suitable for glasses generally treat only the long-range, electrostatic interactions between pairs of atoms. A typical functional form for a two-body potential is the Born-Meyer-Huggins, i.e.,

$$\phi = \frac{e^2}{4\pi\epsilon_0} \frac{Z_i Z_j}{r_{ij}} + B \exp(-r_{ij} / \rho) \quad (1)$$

where the first term represents the Coulomb potential and the second term represents the repulsion potential. The success of such ionic potentials in representing the major features of the silicate glass network is remarkable. Recently, improvement in results has been obtained by using interatomic functions which attempt to include the covalency via the

introduction of explicit 3-body terms [10, 13]. One of a number of such potential forms is that due to Garofalini [13]:

$$\begin{aligned} \varphi = \frac{e^2}{4\pi\epsilon_0} \frac{Z_i Z_j}{r_{ij}} \operatorname{erfc}(r_{ij} / \beta_{ij}) + B \exp(-r_{ij} / \rho) \\ + h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{jk}, r_{ji}, \theta_{kji}) + h(r_{ki}, r_{kj}, \theta_{ikj}) \end{aligned} \quad (2)$$

where the Coulomb potential term of equation (1) is modified to account for long-range Coulomb forces, and

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda_i \exp\left[\gamma_i / (r_{ij} - r_i^c) + \gamma_i / (r_{ik} - r_i^c)\right] (\cos \theta_{jik} - \cos \theta_{jik}^c)^2 \quad (3)$$

if  $r_{ij} < r_i^c$  and  $r_{ik} < r_i^c$ , or equals zero otherwise. Here  $r_{ij}$  is the distance between atoms  $i$  and  $j$ ;  $\theta_{jik}$  is the angle between atoms  $i$ ,  $j$ , and  $k$  whose vertex is at atom  $i$ ; and  $\theta_{jik}^c$  denotes the unconstrained, minimum energy value of the angle. Other symbols denote constants.

Boron-containing glasses have proved challenging to model. The conversion between trigonal and tetrahedral boron-oxygen units, and the reproduction of the boroxyl unit, are stringent tests of interatomic potentials for borate and borosilicate glasses. At present, only one potential model has successfully reproduced the boroxyl grouping [11]. This is important to waste glass modeling, since many waste glasses are of the borosilicate family.

Interatomic potentials for heavy elements have received little attention in the literature. There is currently a need to develop good potentials for both transition metals and actinides, in order to model waste glasses which typically contain such species.

Despite enormous advances in computing technology, simulations are of very small (in macroscopic terms) samples of material and over very short spans of time. Since numerical solution requires timesteps of the order of picoseconds, even a long simulation mimics only a small interval of "real" time. For glasses, the simulation is typically started from an arbitrary arrangement of atoms (often a crystal structure, if the composition being simulated has a crystalline form), is then randomized by simulation at high temperatures (e.g., 6000K), and is then "quenched" by a series of temperature decreases interspersed with equilibration periods. The short duration of the simulation thus imposes extremely high quench rates which are realized in practice only in a few physical processes, such as splat cooling of metals. These aphysical quench rates have some influence on the resulting structure, although the major features of the structure are accurately represented.

Spatial limitations of simulation impact the study of phase separation and of multicomponent systems. The characteristic wavelength for phase separation is of the order of 30-100 nanometers [15], while typical simulation sizes are considerably less than this. Phase separation has been studied nonetheless, by exploiting the ability to calculate thermodynamic quantities from simulation results [15]. Inhomogeneity in composition has been observed on the scale of the simulations themselves [16], which seems to imply that phase separation (or some precursor) could be directly observable via simulation.

The impact of size limitations on the study of multicomponent systems is one of statistics. That is, in simulating a system in which an element represents only a trace quantity, a sufficient number of atoms of that element are required to be present, in order to obtain a

statistically sound representation of the behavior of that element. For example, if 20 atoms of a given type are needed to achieve good statistics for a given property, all components must be present in quantities of at least two mole percent, for a 1000 atom simulation.

## APPLICATION TO WASTE GLASS MODELING

Atomistic simulation has been used to simulate many phenomena of interest in waste glass modeling. Glass homogeneity is key in assessing the durability of waste glass [1]; phase separation studies have already been noted above [15]. Another key issue in waste glass durability is that of water attack on the glass surface. Water-silica interface simulations by Garofalini [17] represent an important step in this area.

Atomistic simulation is currently being used as part of the developmental extension of SRS product and process models, originally formulated for high-level waste glass. In-house simulation software, originally developed for studying gas-metal interactions [18], has been adapted for the study of glass. A unique feature of this software is that simulations can be conducted in a variety of statistical mechanical ensembles; alternate ensembles provide a means of calculating, or calculating more expediently, many thermodynamic quantities not easily computed in the standard microcanonical ensemble (i.e., where the simulation volume, number of atoms, and system energy are all conserved). Currently, two- and three-body interatomic potential functions are being used, although efforts have begun to develop alternate potential functions which should allow a more accurate representation of multicomponent and heavy element-containing systems.

One of the SRS process models is for melt viscosity, which is characterized as a function of temperature and non-bridging oxygen content [1]:

$$\log_{10} \eta = -0.61 + \frac{4472.45}{T[^\circ\text{C}]} - 1.534\text{NBO} \quad (4)$$

NBO, the number of non-bridging oxygens per silicon, is computed as

$$\text{NBO} = \frac{2(\sum_i (M'_2O)_i) + \sum_j (MO)_j + Fe_2O_3 - Al_2O_3 + B_2O_3}{SiO_2} \quad (5)$$

where  $M'$  is an alkaline element and  $M$  is an alkaline earth element. This reflects the conventional glass science view that each alkali cation produces one non-bridging oxygen, while the divalent alkaline earth cations each produce two such non-bridging oxygens. It was found [2] that the fit to experimental data was much improved by reducing the assumed relationship between alkaline earth cations and NBO, i.e.,

$$\text{NBO} = \frac{2(\sum_i (M'_2O)_i) + Fe_2O_3 - Al_2O_3 + \sum_j A_j (MO)_j + B_2O_3}{SiO_2} \quad (6)$$

with

$$A_j = 1.5 \quad \text{for} \quad [MO]_j \leq 0.45$$



$$A_j = 1.2 \quad \text{for} \quad [MO]_j \geq 0.45$$

Atomistic simulation [19] of a series of calcium silicates ( $x\text{CaO} \cdot (1-x)\text{SiO}_2$  with  $x = 0, 0.1, 0.2, 0.3, 0.4,$  and  $0.5$ ) was used to verify the NBO relationship for alkaline earth cations. The simulations confirmed a slight reduction of the NBO content below the theoretical value of two per  $\text{Ca}^{2+}$  cation, but the reduction was too small to be consistent with the  $A_j$  values of equation (6). These results were checked by simulating corresponding sodium silicate systems, where the expected NBO relationship obtained.

From comparison of the simulation results of the  $x\text{CaO} \cdot (1-x)\text{SiO}_2$  series with those of the sodium silicate glass, we infer that the increase in viscosity effect of alkaline earth versus alkali (which is implied by the reduction in the NBO factor shown in equation 6) is due to the higher degree of order that the alkaline earth cation imposes on the relatively disordered glass network. This is shown in Figure 2, where sodium silicate and calcium silicate compositions having equal proportions of cations have been compared. This figure shows the number of oxygen neighbors seen by the Na or Ca cation. For both cases, the sodium ions have a much broader distribution of oxygen neighbors. That is, although there may be a slight preference for one or two configurations (as indicated by the locations of the peaks), the sodium ions occupy a variety of local environments in the glass. In contrast, the calcium cations show a more sharply peaked distribution, implying that the calcium ion has a more definite "preference" for its environment. It therefore imposes more structure on the network, resists changes to that structure, and hence increases the viscosity.

These results suggest that an additional term is needed in equation (4) to represent both the non-bridging oxygen content and the strength of the cation's ability to order its environment. Future simulation work will focus on characterizing this phenomenon in terms of a simple parameter which can be incorporated into the viscosity model. Possible choices of this parameter are the width of the neighbor distribution, or the energy required to alter the local cation environment. These are quantities which are directly obtainable from the simulation results.

## CONCLUSIONS

The molecular dynamics method of simulating the behavior of atoms can provide insight into the structure of materials. A review of the recent literature shows that important waste glass modeling issues are currently being investigated by these means. Simulation is assisting glass process/product model development by SRS for novel applications such as mixed and low-level waste glass and actinide waste glass formulation. Simulation studies of sodium and calcium silicates show that the alkaline earth cation increases the local ordering of the glass network, thus increasing the structural rigidity of the glass. Future work will focus on characterizing this difference in terms of a simple parameter which can be incorporated into an improved process model for glass melt viscosity.

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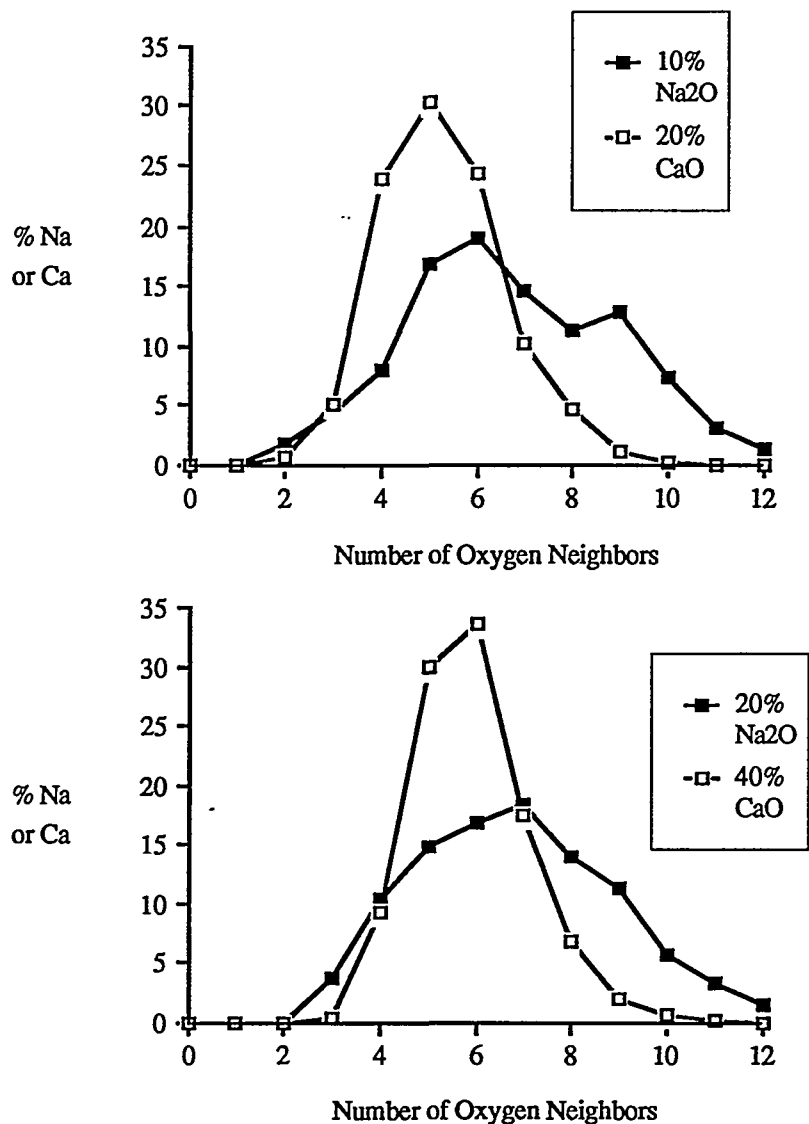


Figure 2. Oxygen coordination around cations in sodium silicate and calcium silicate glass.

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