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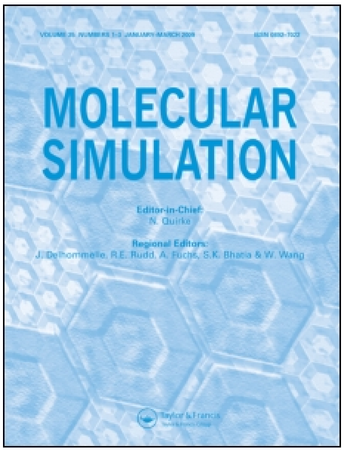

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Towards an understanding of the behavior of silanes on glass: an atomistic simulation study of glass surfaces

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The present work attempts to develop a better understanding of the glass substrates upon which silane molecules are deposited. Experimentally, when a sodium silicate substrate is used, the silane layer does not bind as well compared to an alkaline earth borosilicate glass (AEBS). Molecular dynamics simulated annealing procedures were used to create atomistic models of these glasses and their surfaces. In sodium silicate glass, we see segregation of sodium ions to the surface and formation of sodium-rich regions. For the AEBS glass, we see a more homogenous distribution of ions. Boron, aluminium, silicon and oxygen form a connected framework structure. The barium and calcium ions are distributed throughout the structure and show no evidence of segregation. We speculate the poor performance of sodium silicate, compared to the AEBS, as a silane substrate could be attributed to its compositionally inhomogeneous surface.

Keywords: Amorphous materials; Surface structure; Glass; Molecular dynamics

Introduction

Glass slides, coated with γ-aminopropyl triethoxysilane molecules (GAPS—see figure 1) are currently used in applications such as immobilizing DNA to create microarrays [1] which are widely used in molecular biology. The GAPS molecules are believed to bond covalently to the glass surface via the silane group while leaving a positively charged primary amine group free to attract negatively charged biomolecules such as the phosphate backbone of cDNA.

While there is a good empirical understanding of the glass–GAPS systems, there is relatively little theoretical knowledge of the molecular level processes involved during the coating of the glass surface. Several different proposals have been advanced to explain how GAPS molecules bind to the surface [2–5]. It seems that the precise nature of the interaction is highly dependent on several factors including, but not limited to, the chemical composition of the glass and its surface characteristics such as the roughness, cation concentration and the presence of hydroxyl groups. In addition, work by Eichinger *et al.* [6] on silane binding to the surface of alumina has shown that the barrier for silane polymerization in the presence of water is very low and that it can rapidly occur.

Before the issues of how GAPS and other silane molecules bind to the glass surface is addressed, the nature of the glass substrate upon which the GAPS molecules are deposited must be understood. It is known from experimental studies that the behavior of the coating is different on the surface of sodium silicate glass as opposed to alkaline earth based aluminoborosilicate glasses (AEBS) [7]. Hence, it is imperative that we understand the atomistic structure of the glass substrate. Molecular modeling has been widely used in developing an understanding of the atomic structure of glasses and their surfaces and has proved a powerful tool for numerous systems [8–14]. In the present work, molecular dynamics simulations are used to build surfaces of sodium silicate glass and an AEBS glass in order to improve our understanding of these substrates and thus rationalize the experimentally observed behavior of the silanes on the glass surface. The surfaces, we create do not include the effect of hydroxylation as we would first like to understand the behavior of a fresh fracture surface.

Previous simulations in this area have been primarily done by expert computational chemistry groups and have

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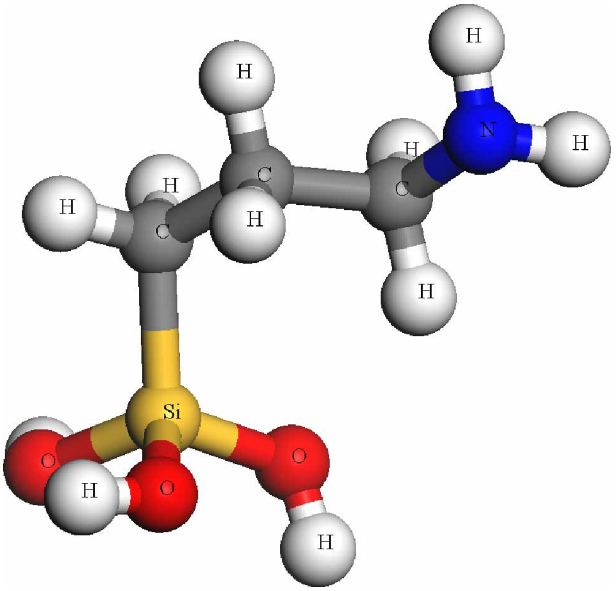

Figure 1. A molecule of GAPS.

typically required significant amounts of time (both in terms of computational time and "research time") to do the studies [15–18]. In an industrial setting, the simulation of such systems has been traditionally avoided due to several reasons: (i) limited computational resources; (ii) the need to produce results quickly either to support the experimental groups developing products or "trouble-shooting" problems that have occurred with existing ones; (iii) a lack of experience with glass systems; (iv) the need to use expert computational chemistry codes. However with the advent of cheaper and better computer hardware and the availability of desktop simulations packages [19], this area is starting to become more accessible for the corporate molecular modeler. While this solves many of these issues, it does not answer the questions on how to do these types of simulations in a straightforward manner. In this work, we present, what we believe to be, a holistic methodology to study such materials in a commercial research setting. Our work is done with commercially available computational tools, on relatively modest hardware.

Modeling approach

Building amorphous bulk materials

The composition of the glasses studied is listed in tables 1 and 2. Typically, the first step in building glass surfaces is to build the bulk amorphous material. We build the amorphous bulk glass by using a simulated annealing scheme, this allows the ions to thoroughly explore conformational space at high temperatures and as the temperature is reduced they come to equilibrium. The procedure consists of three stages: the creation of a periodic cell containing the glass ions; annealing the system; and creating the glass surface (which is also re-equilibrated). Initially, one must first select the fragments to be used as building blocks to create an amorphous cell of the material. The fragments were chosen to be the neutral fragments of the components as listed in tables 1 and 2, in addition, we include Si_2O_4 fragments to produce a reasonable starting distribution of both two and four coordinate silicon atoms which helps to bring the system to equilibrium in a shorter time frame. Such fragments are then packed into a periodic cell at an appropriate density using a Monte–Carlo algorithm [20]. In the present work, a cell containing between 700 and 1000 atoms was built using the appropriate fragment concentration, within a 3D periodic cell at a density of about $2.0\,\mathrm{g\,cm^{-3}}$. Using these parameters, the periodic cell would be approximately $25 \times 25 \times 25\,\text{Å}^3$ in size, which is a sufficient size to ensure that atoms within the cell will not interact with their periodic images in adjacent cells during the annealing process. Such an approach has become standard when studying amorphous polymers.

Table 1. AEBS compositions expressed as mole percent.

AEBS components	*Concentration (cation %)*
SiO_2	55.9
Al_2O_3	18.7
B_2O_3	14.8
CaO	5.3
BaO	5.2

Table 2. Sodium silicate glass compositions expressed as mole percent.

Sodium silicate components	*Concentration (cation %)*
SiO_2	66.6
Na_2O	33.3

Once the cell is built, we use a quenched molecular dynamics approach to optimize the positions of the atoms. This method involves running NVT molecular dynamics (constant number, volume and temperature) at 7000 K for 20 ps, followed by another 20 ps of NPT (constant number, pressure and temperature) molecular dynamics. The purpose of this initial two-stage process is to optimize the ionic positions followed by the cell density during the NPT phase. The system is bought to equilibrium by gradually reducing the temperature in 1000 K steps and re-equilibrating for 20 ps, after each temperature reduction, until it reaches 300 K. This allows the ions to thoroughly explore conformational space at the higher temperatures and as their energy is gradually reduced, they come to low energy metastable positions in the glass. The calculations were performed using the Discover molecular mechanics code [21]. The procedure was automated by means of BTCL script which combines all of these steps into a single Discover input file.

In the present work, a modified version of the cvff_aug forcefield parameter set is used which contains additional parameters for boron. While this forcefield contains no valence terms and is purely based on the non-bonded forces, it has successfully been applied to a range of systems [22–24]. For the Columbic forces, an Ewald [25] summation is used, while a direct cut-off of 12 Å is applied for the Van der Waals forces.

Building amorphous surfaces

The modeling of surfaces requires the use of a technique called the "vacuum slab model". This involves placing a "slab" of material into a 3D cell and then extending one side of the cell (typically, the *C*-axis) such that slabs in neighboring cells will not interact with each other (usually, a distance of 50–60 Å). In addition, the number of atoms in the cell is increased by extending the *A* and *B* directions to create $30 \times 40\,\text{Å}^2$ cell. Thus, each surface will consist of approximately 2000–3000 atoms. A similar simulated annealing protocol is adopted to build the glass surfaces as to those used for building the bulk glass. However, subjecting them to such high temperatures would result in the atoms leaving the surface slab and entering the vacuum. Thus, the samples are initially annealed at 600 K and cooled to 300 K in 100 K steps using 20 ps equilibration times. Such a process allows a relaxation of the ions at the surface to energetically more favorable positions. Considering the materials are amorphous, the surfaces should be built several times to produce a statistically averaged system. Hence, the surface simulated annealing calculation is repeated 10 times, which is a reasonable number of surfaces from which to draw conclusions. Such a modeling procedure can be experimentally likened to the behavior of a fresh fracture surface of glass, where the ions will try and move to their energy minima when the surface is created.

To ensure any results for ion migration or rearrangement were not the result of surface "vaporization", the surfaces were annealed at successively higher temperatures to find the temperature at which this occurred. This was seen to happen at 4000 K, implying the annealed surfaces, we have created are stable and not an artifact of the simulation method.

Results

Once the calculations were complete, several types of analysis of the glass structures were carried out to develop an understanding of the behavior of the glass surfaces at an atomistic level. Each individual property calculated gives some information and can be pieced together to give an overall picture. The analysis is described below:

Structural visualization

The ability to visualize the surface slab is a very powerful tool as it allows the examination of the surface structure; which atoms are at the surface, how they exist at the surface and where they are on the surface. In addition, such analysis can guide the decision as to what further analysis is required.

Diffusion coefficient

During a molecular dynamics run, it is possible to save a trajectory file of the atom positions and velocities as a function of time. Thus, it is possible to map out the movement of ions over the period of the calculation. This trajectory file can be analyzed to give the mean square displacement (MSD) of the ions of interest over a specific period of time. The gradient of the MSD vs. time is the Einstein diffusion coefficient. This property is a good measure of the mobility of individual ionic species in the glass. Knowledge of this property in concert with other properties can help predict future structural changes such as surface segregation and the relative rates at which they may happen. In the present scenario, the MSD is calculated by taking averages over all of the ions in the system, using a time frame of 20 ps (when the ions are at 300 K). This is a relatively short time frame for an accurate prediction of the diffusion coefficient, however, the system size makes longer calculations prohibitive. This being said the average is over a large number of runs and as the primary interest is in the relative mobility of the different ionic species in the system, this value will still provide useful information. Thus, it would be better to treat the results as qualitative rather than quantitative. More detailed description of diffusion simulations in glasses, can be found in the work of Cormack [26] and Garofalini [17] who carry out more extensive studies in this area. In addition, such calculations only give the self-diffusion coefficient of the ions, they do not take into account other types of diffusive behavior occurring over different time and length scales such as glass flow.

Concentration profile

The concentration profile, as the name implies, is a profile of composition or concentration of a species as a function of points along the axes of the periodic repeat unit. Hence for a surface, a profile of the concentration along the axis normal to the surface slab will allow the study of changes in the composition before and after relaxation, e.g. to study surface segregation.

Coordination numbers

The coordination of ions in the system is a good indication of how "polymerized" the glass system is and of what units they are composed. Glass is a metastable material, which consists of framework ions, in which other non-framework ions are distributed. The framework ions will lower their energies by trying to assume coordinations similar to those found in crystalline systems, e.g. silicon will try to be four coordinate and aluminum ions will try to be either four or six coordinate. Thus the number of framework ions that have "non-standard" coordination are good indicators of the stability of the glass. In addition, where such ions are found can be of importance. For example, a large number of three coordinate silicon ions at the surface would imply that such a glass would react more readily with silane coupling agents, than a surface with a large numbers of four coordinate silicon atoms.

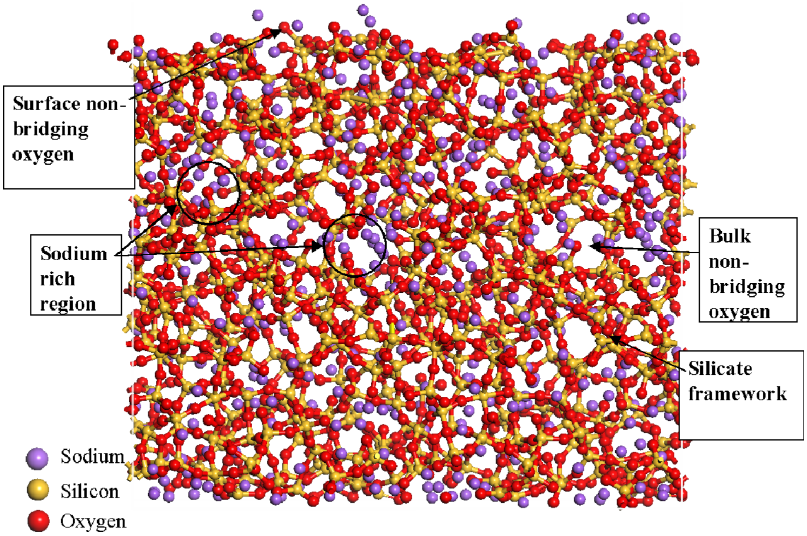

Figure 2. A view of the sodalime glass surface parallel to the *C*-axis. The colour version of this figure is in the online version of this journal.

Surface smoothness

The smoothness of a surface at the atomic level may play a major role in the formation and quality of the monolayers that form upon it. If a surface shows less corrugation, the implication is that it is "flatter" at an atomic level and hence, molecules such as GAPS are more likely to form a uniform monolayer. A quantitative measurement of such a property can be obtained using modeling since, it is possible to calculate the area of the surface at an atomic level. This can be done by using the "free-volume" tool in the Cerius^2 package [27,28]. This tool allows the calculation of VDW surface, solvent surface and the accessible surface for molecules and periodic systems by placing a "probe atom" of a given radius at specific points on a cubic grid around the system. In the present work, we use a probe radius of 2 Å on a grid spacing of 0.15 Å to calculate the accessible surface area. The radius of 2 Å is used as this is roughly the size of silane region in the GAPS molecule. To form a quantitative view of the surface smoothness, this calculated surface area is normalized by dividing it by the area of the simulation cell in the directions parallel to the slab (i.e. by multiple the lengths of the *A* and *B* cell dimensions respectively). The resulting number indicates the degree of smoothness; a value of 1 would imply a perfectly smooth surface on an atomic level (e.g. a metal (111) plane), while values greater or less than 1 would imply a degree of corrugation on the surface.

Sodium silicate

Structure. Simulated annealing results of sodium silicate glass show that silicon and oxygen ions form linked tetrahedra, these act as the primary network formers in the glass. The sodium atoms form clusters throughout the glass, both in the bulk and at the surface. These sodium-rich regions are surrounded by singly coordinated oxygen ions (so-called non-bridging oxygen ions (NBO)). Visually, it can be seen that the sodium ions show some degree of surface segregation. Figures 2 and 3 show an example of a glass surface, from two views, side on and top down, were the network structure of the glass and the sodium-rich regions can clearly be seen. This is consistent with the previous modeling results from Cormack and Huang [18] who used shell model simulations to study bulk sodium silicate glasses as well as the work of Garofalini *et al.* [29,30] who use molecular dynamics to study the surfaces of lithium, sodium and potassium based glass surfaces. In addition, EXAFS studies of cesium and potassium based glasses are consistent with this interpretation [31,32].

Diffusion. The results for the diffusion coefficients for the ions in sodium silicate glass are shown in figure 4. The general trend is very clear in that sodium ions are

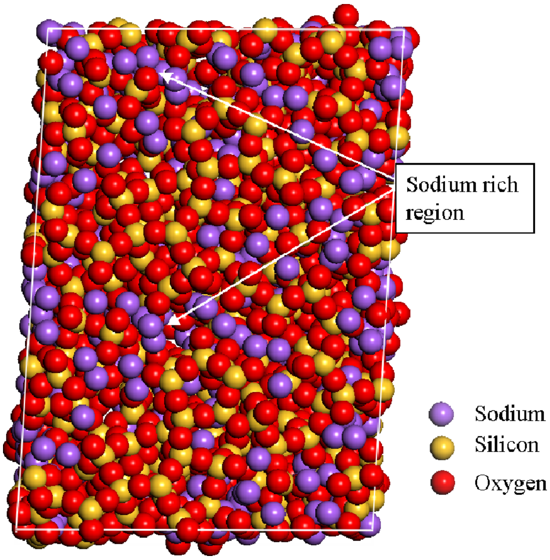

Figure 3. A view of the sodalime surface slab normal to the *A* and *B* axis plane.The colour version of this figure is available in the online version of this journal.

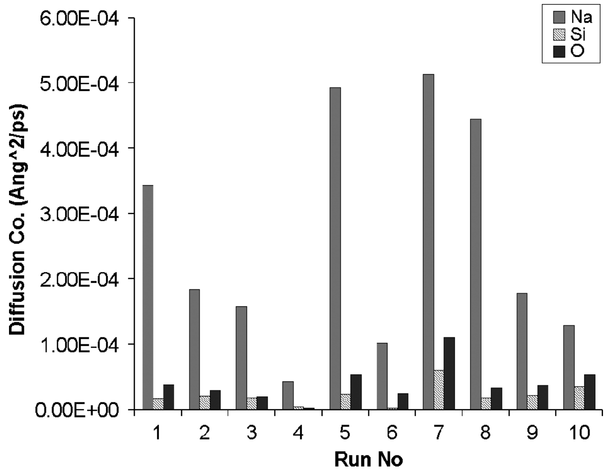

Figure 4. The diffusion coefficients for the ions in sodalime, as a function of run number.

roughly 10 times more mobile than the silicon or oxygen ions. The oxygen ions are a little more mobile than the silicon ions, but both are essentially static on the time frame of the sodium ions. The values are probably underestimates and no doubt, the sodium ion is much more mobile than these values.

Concentration profile. The profiles of the changes in concentration can be seen in figures 5 and 6, which is an example from one of the runs. It is immediately clear that the annealing process encourages the segregation of sodium ions to the surface of the slab. This helps substantiate the conjectures made during the visual analysis of the slabs and analysis of the mean square displacements.

Coordination. The coordination numbers of the bulk glass are listed in table 3. It is clear from these numbers that the glass is made up of a silicate framework in which the sodium ions are dispersed. The majority of the silicon atoms form four coordinate structures. Two thirds of the oxygen ions form bridging atoms between the silicate tetrahedra, which can be seen by their two-fold coordination. The rest are singly coordinated and can be classed as NBO which coordinate with the alkali ions. In fact, from a purely numerical point of view, there are 140 NBO atoms and 140 sodium ions, implying that all the NBO atoms are associated with a sodium ion.

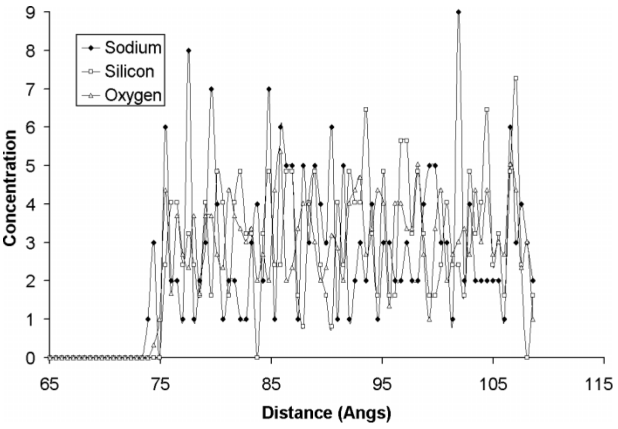

Figure 5. Concentration profile of sodalime glass parallel to the *C*-axis before annealing.

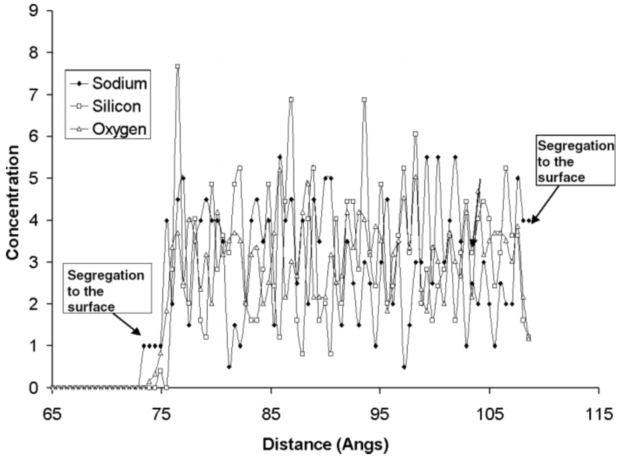

Figure 6. Concentration profile of sodalime glass parallel to the *C*-axis after annealing.

The average ionic coordination for the surface slabs is listed in the table 4. Generally, the coordination for the ions does not change significantly. This is not surprising, if one considers the size of the surface slab. It is about 35 Å in size and hence, the number of ions at the actual surface will be smaller than the number of ions in the bulk. However, the results do prove useful in that one can pick up subtle changes in the coordination as a result of there being a surface. There is about a 3% increase in both the numbers of three and five coordinate silicon atoms. Likewise for oxygen, there is a small increase in the amount of zero coordinate oxygen (1%) and from the decrease in singly coordinated oxygen, these zero coordinate ions must have been NBO atoms that moved further into the sodium-rich regions. The three coordinate silicon ions no doubt act as coupling points for silane molecules.

Surface smoothness. The results for the atomic smoothness of the sodium silicate surfaces is shown in table 5. The results indicate sodium silicate does have a rumpled surface, with an average smoothness of about 1.26

Alkaline earth borosilicate glass (AEBS)

Visualization. The resulting structures from the simulated annealing of AEBS glass show a different structure compared to sodium silicate glass, with many more of the

Table 3. Ionic coordination (in %) for bulk sodium silicate glass.

Coordination	*0*	*1*	*2*	*3*	*4*	*5*	*6*
Si	0	0	0	0	99.43	0.57	0
O	0	33.10	66.90	0	0	0	0
Na	100	0	0	0	0	0	0

Table 4. Average ionic coordination (in %) for surfaces of sodium silicate glass.

Coordination	*0*	*1*	*2*	*3*	*4*	*5*	*6*
Si	0	0	0	2.6	94.21	3.17	0.19
O	0.94	32.82	67.04	0.14	0	0	0
Na	100	0	0	0	0	0	0

ions involved in the formation of the framework including: aluminum, boron, silicon and oxygen. The alkaline earth ions (calcium and barium) show a uniform distribution through the material and do not seem to cluster like the sodium ions in sodium silicate glass. Figures 7 and 8 shows an example of the AEBS glass surface, with views parallel and perpendicular to the *A* and *B* axis plane. The figures show a highly networked structure akin to a highly cross-linked polymer resin. The surface shows a predominance of the network forming ions, with no sign of the alkaline earth ion segregation to the surface. However, it must be kept in mind that the concentration of these ions is approximately a third of that in the sodium silicate glass. Hence, clustering and segregation may occur at higher concentrations. The aluminum and silicon cations are known to form four coordinate tetrahedra with oxygen ions. Boron can form both three and four coordinate structures. Presumably, ions that form four coordinate structures relatively easily are suitable coupling points for the silane reagents. Another point of note is that surface is much smoother and shows a greater similarity to the structure of bulk AEBS.

Diffusion. The MSD’s for AEBS have been analyzed to give the diffusion coefficients. These are plotted in figure 9, to aid comparison the same scale is used as for figure 4. The results seem less conclusive than the results for sodium silicate, in that no one species is consistently more mobile than another. However, it does show that in general, the ionic species in AEBS are less mobile than in sodium silicate, with the exception of run 5 which we believe to be a “rogue” point. Also, it shows that the diffusion coefficients of the framework species are closer to each other. The alkali ions, calcium and barium, are more mobile. However, from the graph it would be hard to give a quantitative number on how much more mobile. The most likely reason for the poor quality of these results is that as the ions are highly networked, they are practically immobile on the timescale of our annealing simulations. Thus to get better quality data, we would have to run the calculations for a much longer time, possibly hundreds of pico-seconds to get any reliable data. No doubt, the result of longer calculation would essentially give much better quantitative values. However, the overall conclusion would be the same, the framework ions will have very small diffusion coefficients and the calcium and barium ions will be more mobile, but not as mobile as the alkali ions in sodium silicate.

Table 5. Calculation of surface smoothness for sodium silicate.

Run number	*Surface area* ($\AA^2$)	*Unit cell area* ($\AA^2$)	*Curvature*
1	2850.44	2223.07	1.28
2	2765.62	2223.07	1.24
3	2823.09	2223.07	1.27
4	2791.06	2223.07	1.26
5	2761.21	2223.07	1.24
6	2763.82	2223.07	1.24
7	2793.28	2223.07	1.27
8	2875.34	2223.07	1.29
9	2781.4	2223.07	1.25
10	2821.69	2223.07	1.27
Average	2802.70	2223.07	1.26

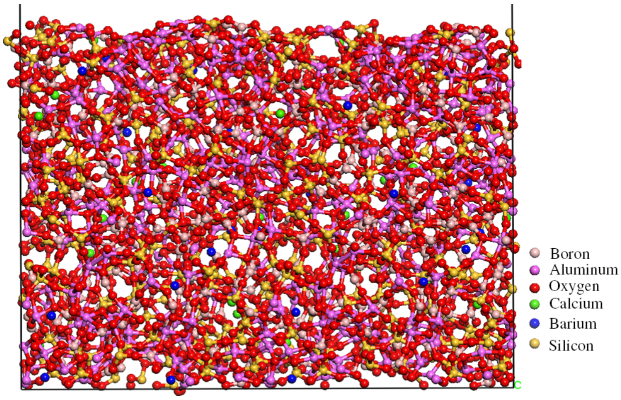

Figure 7. A view of the AEBS glass surface parallel to the *C*-axis. See online version of journal for colour figure.

Concentration profile. Given that there are more species in the AEBS glass, the concentration profiles are more complicated and features are more difficult to discern. The concentration profile before annealing shows that there are several peaks of high alkaline earth concentration and an essentially continuous distribution of the network forming ions through the material (an example is shown in figure 10). The annealing process essentially makes the glass slightly more homogenous in composition (figure 11), but on the whole it remains relatively

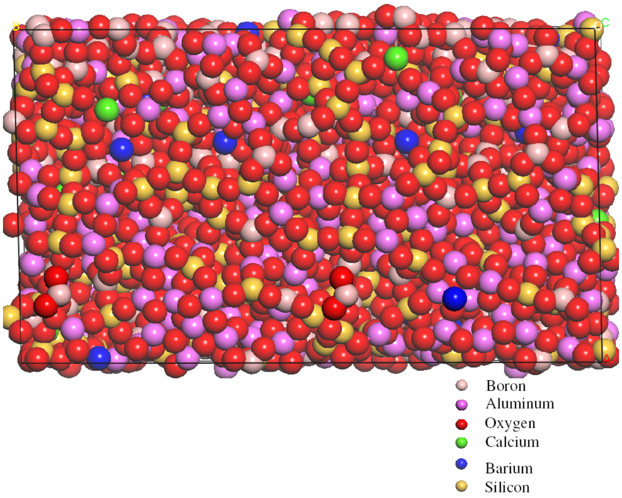

Figure 8. A view of the AEBS surface normal to the *A* and *B* axis plane. Note the homogeneity of the surface. See online version of journal for colour figure.

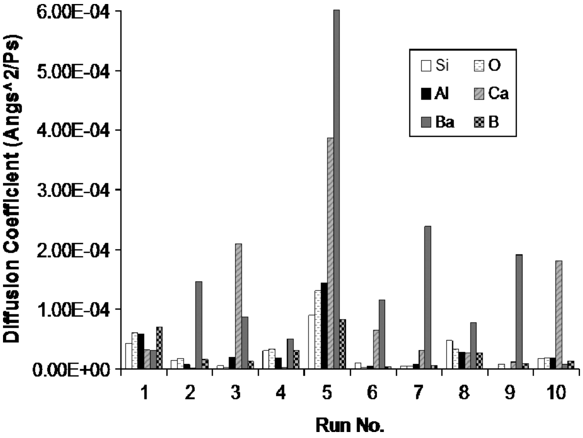

Figure 9. The diffusion coefficients of the ions in the AEBS glass, as a function of run number.

unchanged. The network forming ions show very little change in their concentration during the annealing process. This is not surprising given, they are essentially static on the annealing timescale; implying very little segregation of any ions to the surface. As the individual alkaline earth concentration is much lower than in the sodium silicate glass, their peaks represent one or two ions as opposed to large concentrations of ions. Hence, one must be careful when drawing general conclusions. However, the annealing process reduces the two high concentration calcium sites and creating more sites with lower concentrations. Barium behaves in a similar way and the ions become more dispersed throughout the lattice. Instead of isolated sharp peaks in the concentration profile, we see more peaks with lower concentrations.

Coordination. The coordination of the bulk silicon ions is very similar to that of sodium silicate glass with over 99% being in four coordinate positions (table 6). Similarly, the majority of oxygen ions adopt a two coordinate bridging structure. However, unlike sodium silicate, there are virtually no single coordinate ions, with approximately 30% of ions being three coordinate, which is commensurate with observation of an extensive network structure within the glass. Boron and aluminum show high coordination numbers as they are also part of the network structure as well. The aluminum ions show a predominance of four coordinate structure, which is analogous to aluminium coordination in aluminosilicate materials. Unusually, there is very little octahedral coordination (the other stable coordination state for aluminum), which can be explained in terms of the significant amount of five coordinate aluminum. These five coordinate species are possibly frustrated coordination states; ions that were going from a tetrahedral to octahedral coordination, but were trapped in the five coordinate state during the annealing process. Hence, as also indicated in the diffusion studies, the highly networked structure of AEBS prevents the aluminum ions from migrating to their global minima. This ratio may change if the annealing was run for longer. This being said, NMR studies of AEBS glasses [33] do show significant amount of five coordinate aluminum. Boron has a roughly 2:1 split of three and four coordinate ions, both of which are also observed in the NMR studies. The average results for the surface slabs are shown in table 7. The silicon ions, like those in sodium silicate, show increased three and five coordinate ions with similar amounts becoming three and five coordinate. The aluminum ions show about a 3.5% increase in the number of three coordinate ions, which must be a result of under coordinated tetrahedral sites at the surface, with a resulting decrease in the amount of four coordinate aluminum. Analogously, the boron ions also show an approximately 3.5% increase in the three coordinate concentration, which corresponds to a similar decrease in the four coordinate concentration. This would imply that these ions are at the surface of the slab.

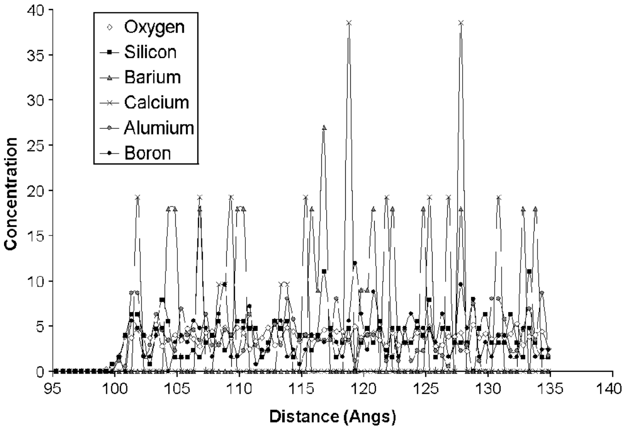

Figure 10. Concentration profile for the AEBS glass parallel to the *C*-axis before annealing.

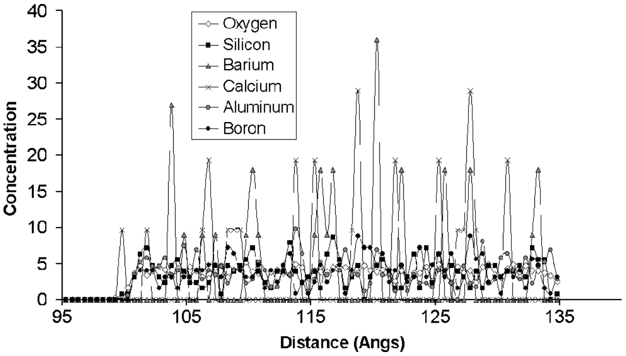

Figure 11. Concentration profile for the AEBS glass parallel to the *C*-axis after annealing.

Table 6. Ionic coordination (in %) of bulk AEBS glass.

Coordination	*0*	*1*	*2*	*3*	*4*	*5*	*6*
Si	0	0	0	0	99.29	0.71	0
Al	0	0	0	0.53	71.28	25	3.19
O	0	0.49	71.05	28.40	0.37	0	0
Na	0	0	0	0	0	0	0
Ca	100	0	0	0	0	0	0
Ba	100	0	0	0	0	0	0
B	0	0	0	68.24	31.76	0	0

Table 7. Average ionic coordination (in %) of AEBS glass surfaces.

Coordination	*0*	*1*	*2*	*3*	*4*	*5*	*6*
Si	0	0	0	1.36	95.81	2.83	0
Al	0	0	0	3.96	68.33	25.46	2.27
O	0	0.91	70.13	28.68	0.28	0	0
Ca	100	0	0	0	0	0	0
Ba	100	0	0	0	0	0	0
B	0	0	0.3	71.94	27.91	0	0

Surface smoothness. Table 8 shows the surface smoothness results for AEBS and indicates that AEBS is about 4% smoother than sodium silicate. This difference is small, but possibly significant. Hence to test this hypothesis further, one would have to create more surfaces of the present system and to examine other glass surfaces.

Summary and discussion

The results from the previous sections show that within sodium silicate glass, the silicon and oxygen ions form a framework in which the sodium ions are dispersed. These form sodium-rich regions which are surrounded by non-bridging oxygen atoms. These characteristics are seen both in the bulk and on the surface of the glass. In fact, these clusters can interlink to form channel structures and can extend from the surface into bulk. This is also seen in potassium and rubidium based glasses [34,35]. Analysis of the concentration profiles shows that sodium migrates to the surface of the slab during the annealing process. This is further reinforced by the diffusion coefficient calculations which show sodium is the most mobile of the ions. Thus, over time the sodium concentration at the surface will increase and concentrate in specific areas.

The AEBS glass shows a highly networked structure with boron, silicon, aluminum and oxygen forming the framework, in which the barium and calcium ions are dispersed. The surface structure is very homogenous and similar in structure to that of the bulk. The concentration profiles show no major change during the annealing process, implying surface segregation of the ions over a much longer timescale, if at all. The diffusion studies show the framework ions are essentially static on the time scale of the simulation and the alkaline earth ions do not migrate extensively. This is not to say that the ions do not diffuse, it is just that if they do, they do so on a longer timescale and certainly not at the same rate as the sodium silicate glass. The coordination studies show that the cations at the surface are under coordinated and are probably good points for the binding of silanes. An analysis of the atomic smoothness of the surface shows that it is marginally smoother than the sodium silicate surface, however, further studies would have to be done to test this theory.

Table 8. Calculation of surface smoothness for the AEBS glass.

Run number	*Surface area* ($\mathring{A}^2$)	*Unit cell area* ($\mathring{A}^2$)	*Curvature*
1	3041.10	2510.41	1.21
2	3041.69	2510.41	1.21
3	3058.33	2510.41	1.22
4	3132.60	2510.41	1.25
5	3069.35	2510.41	1.22
6	3035.06	2510.41	1.21
7	3103.87	2510.41	1.24
8	3067.25	2510.41	1.22
9	3011.75	2510.41	1.12
10	3100.76	2510.41	1.24
Average	3066.18	2510.41	1.22

The better performance of AEBS as a substrate for GAPS can be rationalized in terms of the following:

i) The surface composition of AEBS does not change significantly over time compared to that of sodium silicate where the sodium rapidly diffuses to the surface. This may disrupt the binding of the GAPS layers.
ii) The surface of AEBS is homogenous and shows no clustering of any of the species. On the other hand, the sodium silicate surface is inhomogenous in which it has regions of high sodium concentration. Thus, affecting the uniformity of any silane surface layer;
iii) Boron, aluminum and silicon ions are present on the surface of AEBS. These are known to be tetrahedrally coordinated by oxygen. In addition, analysis of their coordination for the bulk and surface structures shows a slight increase in the three coordinate state compared with the bulk. Thus the ions present at the surface are under coordinated and hence, may couple to GAPS to form four coordinate structures. Conversely, in sodium silicate, it would only be possible for the GAPS to bind to silicon atoms.

These conclusions are lent weight by the observations of Fowkes *et al.* [36] who studied the behavior of PMMA on the surfaces of glass. They found that PMMA films peeled off more easily on sodium glasses than on alkali free glasses. In addition, they found that they could ensure strong adhesion of PMMA to sodium silicate by using an acid rinse, however, this only had a finite time which could be attributed to the migration of sodium ions to the surface.

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