The initial stages of bioglass dissolution: a Car–Parrinello molecular-dynamics study of the glass–water interface

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The initial dissolution stages following implantation of a biomaterial in a physiological environment are critical for its bioactive properties. Car–Parrinello molecular-dynamics (CPMD) simulations of the interface between the 45S5 bioglass surface and liquid water have been carried out to investigate these processes. The analysis of a 40ps CPMD trajectory has highlighted the potential mechanism of Na+ / H+ exchange, leading to formation of surface silanols through water dissociation. Moreover, by comparing the properties of water layers arranged at different distances from the glass surface, we discuss the way in which the particular structure and composition of the bioglass surface affects the hydrogen-bond network and orientation of water in its close proximity.

Keywords: bioglass; molecular-dynamics simulations; dissolution

1. Introduction

When a surface-active bioactive silicate glass is immersed in an aqueous medium, after implantation of the biomaterial in a physiological environment, a sequence of inorganic stages leads to the partial dissolution of the glass (Hench 1998; Tilocca 2009). This is a key step towards the bone-bonding and tissue-regeneration ability of these materials: on one hand, it has been shown that a fast initial dissolution results in a shorter time needed to form a stable bonding interface with hard (bone) and soft (muscle) tissues (Peitl et al. 2001); on the other hand, it has been recently found that some bioactive properties, namely the ‘osteoproducive’ ability to promote growth of new tissue away from the glass surface, depend on the release of critical amount of ionic species in the surrounding medium, following the initial dissolution (Xynos et al. 2001). Unlike fully resorbable biomaterials, such as phosphate glasses (Knowles 2003), bioactive silicate glasses do not completely dissolve shortly after implant (Hench 1998): the initial dissolution self-passivates

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the surface against further degradation (Clark et al. 1976), and the presence of a stable interface is essential to support the deposition and growth of new tissue. The relevance and the complex nature of the processes occurring at the glass–liquid interface highlight the need of fundamental investigations of this region (Tilocca 2010a). Unresolved issues are the nature and strength of active sites found on the surface, the structure of the hydration layers and their role in the surface dissolution. Recent Car–Parrinello (CP) simulations (Car & Parrinello 1985) have started to shed light on these subjects (Tilocca & Cormack 2008, 2009). This computationally demanding ab initio approach, employing periodic supercells and finite-temperature molecular dynamics (MD), represents a suitable way to investigate the highly heterogeneous energy landscape of a multicomponent glass surface (Tilocca 2010a). In particular, the strength of selected surface sites can be probed by examining their interaction with an isolated water molecule (Tilocca & Cormack 2008), as well as with an extended film mimicking a bulk solvent (Tilocca & Cormack 2009). These recent simulations have highlighted the role of exposed Na cations in coordinating water and promoting solvent penetration in the earliest stages of the dissolution mechanism. Another factor, also emerged from these simulations, is the unusual kinetic stability of small silicate rings (compared with those found on the surface of amorphous SiO2), which confirms their potential role as templates for adsorption and growth of the bone-bonding interface (Sahai & Anseau 2005; Bolis et al. 2008; Tilocca 2010a).

In the present work, we look in more detail at how water molecules are organized near the surface, focusing on the hydrogen-bond (HB) connectivity and its effect on the coordination and mechanism of release of Na.

2. Computational methods

CPMD simulations were performed with the QUANTUM ESPRESSO (Giannozzi et al. 2009) CP code. The electronic structure was treated within the generalized gradient approximation (GGA) to density-functional theory (DFT), through the Perdew–Burke–Emzerhof exchange-correlation functional (Perdew et al. 1996). Core-valence electronic interactions were represented through Vanderbilt ultrasoft pseudopotentials (Vanderbilt 1990), explicitly including Na and Ca semicore shells in the valence. A plane-wave basis set with cutoffs of 30 and 240Ry for the smooth part of the wave functions and the augmented charge was employed, with k-sampling restricted to the Γ point. A similar computational set-up has often been employed for modelling water adsorption on oxide surfaces (Mischler et al. 2005; Adeagbo et al. 2008; He et al. 2009). Using the deuterium mass for hydrogen allowed us to effectively decouple ionic and electronic degrees of freedom (Marx & Hütter 2000) with a larger fictitious electronic mass (700 atomic units), which in turn permits a longer time step (0.17fs).

A slab model of the surface was cut from a bulk sample of the 45S5 bioglass composition (45.7 SiO2 : 24.3 Na2O : 27.1 CaO : 2.9 P2O5 mol%), obtained through a CPMD melt-and-quench of a periodic cubic box containing 32 SiO2, 17 Na2O, 19 CaO and 2 P2O5 formula units at the experimental density (Tilocca 2007). A free surface was exposed by doubling one of the sides of the volume-optimized supercell and keeping three-dimensional periodic boundary conditions on the resulting orthorhombic cell. A vacuum region thus separates the top face of
the slab from the periodic image of the bottom face, which is fixed to its bulk-like geometry. After relaxing the dry slab, we filled the gap with 81 molecules extracted from a CPMD model of liquid water (with a further small adjustment of the vertical separation). Now, focusing on the water layers closer to the relaxed face, the thickness of the gap (approx. 18 Å) ensures that these molecules are only marginally affected by the periodic image of the opposite (unrelaxed) face: we can thus assume that the molecules in the first 10 Å above the surface represents a realistic sample of interfacial liquid water. Whereas small amounts of moisture can be adsorbed on the as-created bioglass surface before implantation, it is unlikely that any significant corrosion or degradation of the bioglass surface occurs before effective contact with a bulk aqueous environment: for instance, the initial step of the bioactive process, involving Na/proton exchange with the solution, can only proceed through contact with an aqueous medium. Therefore, assuming that the properties of the interface are not affected by the presence of a small fraction of pre-adsorbed water, the dry surface represents a suitable and reproducible model to study the bioglass–liquid-water interaction.

The fully hydrated system contained 442 atoms and 1952 electrons. A room-temperature CPMD trajectory of approximately 40 ps was carried out in the constant number of particles, volume and temperature ensemble using a single Nosè thermostat, and the first 10 ps were discarded from the analysis.

3. Results and discussion

A snapshot of the glass–water interface, extracted from the CPMD run, is shown in figure 1. The two most relevant structural features of the surface are already evident from the picture: (i) the open nature of the bioglass surface, which reflects the high fragmentation of the bulk silicate network, in turn resulting from the low-silica content of these materials (Tilocca & Cormack 2007; Tilocca 2010a) and (ii) the high amount of exposed Na cations, in direct contact with the water layer (Jallot et al. 2001; Tilocca & Cormack 2009). A more quantitative analysis is provided by the vertical profile of the number fraction of the different species, shown in figure 2. The marked increase in the Na fraction above \( z = 5 \) Å results in a net predominance of O (mostly non-bridging oxygens; NBOs), Na and Si atoms in the top portion of the surface, where a significant water fraction is also observed. This shows that water can significantly penetrate the as-created bioglass surface, and this effect seems to be correlated with the Na enrichment in this region. Favourable \( \text{H}_2\text{O–Na}^+ \) and \( \text{H}_2\text{O–Ca}^{2+} \) interactions on this surface had been suggested by previous DFT energy optimizations (Tilocca & Cormack 2008): the calculated adsorption energy of a single water molecule coordinated to Na and Ca exposed on different surface sites ranged between 0.6 and 1.3 eV. While the broad range of adsorption energies reflects the widely heterogeneous landscape met by a water molecule on this surface, the strong Lewis acidity of all exposed network-modifier cations makes them more favourable as coordination sites than the siloxane portion of the surface. Putting this effect together with the composition of the hydrated surface in figure 2, one can conclude that the main water–surface interaction at the initial interface involves water coordination by NBO\( ^{–}\)–Na\(^{+}\) pairs, whereas Ca\(^{2+}\) ions have a minor role in the initial stages of surface hydration.
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Figure 1. A snapshot of the bioglass–water interface, extracted from the CPMD trajectory. The phosphosilicate network (bottom) is represented as yellow/red ball-and-stick, with Na and Ca cations as green and brown spheres, respectively. Dashed lines highlight HBs.

Figure 2. Vertical ($z$) profile of the fraction of atomic species contained in slices 2 Å thick, averaged over the CPMD trajectory. The centre of the slab model of the surface roughly corresponds to $z = 0$. Black circles, glass O; red squares, Si; light green diamonds, P; dark blue triangles, Na; yellow inverted triangles, Ca; light blue asterisks, water O; violet plus symbols, NBO; dark green crosses, BO.

and dissolution. Direct inspection of the CPMD trajectory showed that the strong NBO–water–Na interaction can result in water dissociation with the formation of a silanol group, according to the reaction

$$\text{Si} – \text{NBO}^– – \text{Na}^+ + \text{H}_2\text{O} = \text{Si} – \text{NBO} – \text{H} + \text{NaOH}.\quad (3.1)$$
A silanol formed as a result of this process is visible in the snapshot of figure 1. The resulting \( \text{OH}^- \) is initially associated to the Na cation, but the trajectory also shows that the \( \text{OH}^- \) charge can be transported elsewhere in the liquid by a sequence of rapid proton transfers along water molecules (Tilocca & Cormack 2009). On the bioglass surface, the close association with a Lewis acid such as Na\(^+\) appears thus necessary to convert an exposed NBO into a silanol group through water dissociation. As additional Na and eventually Ca cations are transported from the bulk to the glass surface, they can likewise assist the protonation of the remaining NBOs: complete protonation of all the initially exposed NBOs can probably be expected on this basis, even though it is not observed on the relatively short 40ps time scale of the CPMD run. The overall effect of reaction (3.1) is the Na\(^+\)/H\(^+\) exchange between the glass and the solution, resulting in increased local alkalinity, which is in turn considered important to promote further degradation of the glass network through breaking of Si—O—Si bridges (Hench 1998).

The open nature of the 45S5 surface somewhat complicates the exact identification of NBOs, which will be protonated, because in this system, water molecules can, in principle, reach and dissociate at NBOs located well below the top of the surface (Tilocca 2010). The extent of this penetration cannot be determined \textit{a priori}, and therefore, the number of protonated NBOs must be estimated based on an arbitrary cutoff separating ‘active’ and ‘inactive’ NBOs. Based on figure 2, denoting water penetration at least in the surface region above \( z = 5 \text{ Å} \), the total number of NBOs found in this region provides a lower limit of approximately 4nm\(^{-2}\) to the final surface density of silanol groups in the fully hydrated system.

The effect of the glass surface on the structural properties of the hydrated water can be examined by comparing the structure of the water molecules in direct contact with the surface (‘surface water’; SW) and those found at higher vertical distances from the surface (‘bulk water’; BW). The \( z \)-profiles in figure 2 allow us to assign water molecules within the \([5 \text{ Å} < z < 10 \text{ Å}]\) layer as SW, and those with \([10 \text{ Å} < z < 15 \text{ Å}]\) as BW; in other words, SW molecules access regions where also atoms belonging to the glass can be found, whereas no glass atoms are present in the BW layer. The water–water radial distribution functions (rdfs) for SW and BW are shown in figure 3. When comparing the rdfs calculated in the two regions, one should take into account the non-spherical and inhomogeneous distribution of water surrounding molecules in a thin rectangular slice: for instance, no BW is found below the SW layer; therefore, the average number of water molecules resident in each layer and the corresponding limit homogeneous density were used to normalize the rdfs in figure 3.

Notwithstanding the tendency of the adopted computational framework to produce over-structured rdfs and overestimate the number of HBs in room-temperature liquid water (Sit & Marzari 2005; Todorova et al. 2006), the relative trends examined here can be considered accurate and representative. The SW and BW rdfs are rather similar, with the intermolecular O—O and O—H peaks of the SW at slightly shorter distances, denoting stronger HBs involving these molecules. This small strengthening of water–water HBs close to the surface can be further investigated by separately calculating the HB statistics of SW and BW. A geometrical definition of HB was used (Tilocca & Selloni 2004a): two molecules were considered linked by an HB when their O—O distance was less than 3.3 Å,

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Table 1. Hydrogen-bond statistics. $n_{HB}$ is the average number of hydrogen bonds per molecule; $< R_{OO} >$ and $< R_{OH} >$ (Å) are the mean O–O and intermolecular O–H length of H-bonded pairs. The SW and BW columns show the overall HB statistics for SW and BW molecules; for water–water interactions, these are further decomposed to analyse HBs between two SW molecules (SW–SW), an SW and a BW molecule (SW–BW), and two BW molecules (BW–BW). Standard errors are quoted in parentheses.

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<tr>
<td>$n_{HB}$</td>
<td>1.88</td>
<td>1.25</td>
<td>0.63</td>
<td>2.48</td>
<td>3.56</td>
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<td>$&lt; R_{OO} &gt;$ (Å)</td>
<td>2.80</td>
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<tr>
<td>$&lt; R_{OH} &gt;$ (Å)</td>
<td>1.83</td>
<td>1.81</td>
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$^a$n_{HB}(BW)$ in the last column also includes HBs between a BW molecule and molecules located above the BW slice, hence $n_{HB}(BW) = [n_{HB}(SW–BW) + n_{HB}(BW–BW)]$.

the OH intermolecular distance was less than 2.4 Å and the OOH angle between the O–O vector and the covalent OH bond was less than 30°. The results of the HB analysis are reported in table 1. Whereas a molecule in the BW region is H-bonded to 3.6 other water molecules on average, the close proximity of the surface reduces the number of water–water HBs for SW molecules by about a half. While some of the lost water–water HBs are balanced by analogous water–surface interactions, the total number of HBs formed by an SW molecule is significantly lower than BW: only approximately 2.5 HBs/molecule in total, including 0.6 HBs/molecule formed with the glass surface. The previous discussion suggests that residual interactions (assuming a pseudo-tetrahedral water coordination) are represented by Na$^+$–O(H$_2$) coordination; as a matter of fact, the O$_{SW}$–Na$^+$ coordination number, calculated by integrating the corresponding rdfs (not shown) up to the first minimum, is 0.8. Therefore, the HB statistics show that the reduced water–water coordination in the surface region is partially balanced by HBs with surface NBO (or NBO–H), and by coordination to Na$^+$. Furthermore, table 1 shows that the small strengthening of HBs in the surface region, inferred from the rdfs, originates from individual HBs between two SW being stronger than those between an SW and a BW, and than those between two BWs. Whereas the interaction with the surface atoms probably plays a role in it, further investigations (for instance of the electronic-charge rearrangements induced upon water contact with the surface) are needed to identify the source of this effect.

The reduced availability of HB partners in the surface region has other structural consequences for the water molecules located there: the distribution of the angle $\theta$ formed by the molecular bisector and the surface normal ($z$-axis) is shown in figure 4 for SW and BW molecules. SW is oriented with the molecular dipole roughly aligned (with an approx. 30° tilt) to the surface normal: the parallel alignment, with the molecular dipole pointing up (away from the surface)
is preferred, whereas the secondary peak at $150^\circ$ arises from water molecules with their dipole pointing down, towards the surface. On the other hand, the most common orientation for BW molecules is ‘complementary’ to the SW ones, with their molecular dipole roughly perpendicular to the surface normal, and a net corresponding decrease in the probability of orientations with the molecular dipole pointing up or down. This pattern can be interpreted on the basis of the reduced availability of HB partners (acceptors) for the SW molecules, which forces them to direct one hydrogen upward (towards the BW molecules) or downward.
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(towards surface NBOs). Because the oxygen of dipole-up SW molecules is frequently coordinated to an Na cation, these orientations are favoured by the initial abundance of Na cations in the glass surface. A BW molecule in the region above SW can either accept an HB from the dipole-up SW, or donate an HB to the dipole-down SW, and figure 4 shows that these configurations involve \( \theta \) angles around 90°. Therefore, even though more HB partners surround BW molecules (table 1), the structured distribution of the orientation of the SW partners induces a corresponding ‘complementary’ anisotropy also in the BW distribution.

4. Conclusions

The high NBO:BO ratio of the bulk 45S5 bioglass composition, with its low SiO\(_2\) content, results in a marked fragmentation of the silicate network. This leads to a fast initial release of ionic dissolution products upon contact with a physiological (aqueous) medium, which is one of the keys to the bioactive behaviour of these materials. The present \emph{ab initio} simulations provide a high-resolution view into the structure and reactivity of the bioglass–liquid-water interface.

We have shown that the initial Na\(^+\)/H\(^+\) exchange at the interface involves water dissociation at an Na\(^+\)–NBO\(^-\) pair, with release of the Na cation from the surface: because transport of further Na\(^+\) ions from the bulk glass to the surface is thus essential to promote complete protonation of surface NBOs, additional CPMD simulations are currently addressing Na migration in these materials (Tilocca 2010b). Moreover, the effect of surface interactions on the water structure and connectivity has been investigated; the relatively low availability of favourable targets for HB interactions on the surface significantly affects water coordination in this region. Na cations partially enter the coordination sphere of an SW, and the reduced density of suitable HB acceptors also determines the preferential upward or downward orientation of water dipoles observed in the surface region, which in turn appears to influence the orientation of the water molecules immediately above them. It is interesting to note how, in spite of the low density and disordered nature of the 45S5 surface, its effect can still be transmitted to molecules not in direct contact with it, as was found for dense crystalline oxide surfaces (Tilocca & Selloni 2004b). Moreover, we found that whereas the overall HB connectivity decreases in the surface region, the strength of individual HBs increases: further calculations are needed to address the electronic and dynamical causes of these effects.

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References


