

## REVIEW ARTICLE OPEN

## Atomistic computer simulations of water interactions and dissolution of inorganic glasses

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Computer simulations at the atomistic scale play an increasing important role in understanding the structure features, and the structure–property relationships of glass and amorphous materials. In this paper, we reviewed atomistic simulation methods ranging from first principles calculations and ab initio molecular dynamics (AIMD) simulations, to classical molecular dynamics (MD), and meso-scale kinetic Monte Carlo (KMC) simulations and their applications to study the reactions and interactions of inorganic glasses with water and the dissolution behaviors of inorganic glasses. Particularly, the use of these simulation methods in understanding the reaction mechanisms of water with oxide glasses, water–glass interfaces, hydrated porous silica gels formation, the structure and properties of multicomponent glasses, and microstructure evolution are reviewed. The advantages and disadvantageous of these simulation methods are discussed and the current challenges and future direction of atomistic simulations in glass dissolution presented.

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The corrosion or degradation of glasses in aqueous solutions are critical in a number of engineering and technological processes ranging from microelectronic packaging, glass reaction chambers, and the immobilization of nuclear waste materials, as well as in healthcare and biomedical fields such as dissolution of inhaled glass fibers and bioactive glasses for biomedical applications. In particular, immobilizing radioactive waste in borosilicate glasses is widely accepted as a preferred method to treat nuclear waste materials generated from civilian and military sources. This process, also known as vitrification, is a critical component of the cycle of nuclear energy to combat global environmental and energy challenges. Researchers from around the world have extensively invested in understanding glass corrosion in an effort to predict the long-term stability and release rate radionuclides to the environment during nuclear waste storage.<sup>1,2</sup>

Various mechanisms for glass corrosion have been proposed and despite intensive experimental investigations with advanced characterization techniques results are unclear. It is generally accepted that the corrosion of glass consists of a set of complex processes including hydration, hydrolysis, and ion-exchange that are coupled during glass dissolution. The initial stage is inter-diffusion of proton or hydronium ions from the solution with sodium or other alkali ions in the glass.<sup>3</sup> This is followed by the hydrophilic attack of water on the Si–O–Si or Si–O–Al linkages that lead to hydroxylation of the silicate glass network. The remaining hydrolyzed glass skeleton then undergoes condensation and repolymerization to form the hydrated nanoporous silica rich gel layer which can be protective, decreasing dissolution to a residual rate.<sup>4–6</sup> The morphology of the gel layer, such as thickness, pore structure, and chemical composition, depends on the original glass composition and the pH, temperature, and composition of the solution. The resulting alteration layer is thus composed of an inter-diffusion region, an amorphous hydrated layer, and the

crystalline reaction product layer schematically shown in Fig. 1.<sup>7</sup> A more accurate picture of the regions has been obtained by advanced characterization techniques such as atom probe tomography on corroded glasses<sup>8,9</sup> so that the nature of the alteration layer and related interface morphology can be more clearly understood.

Despite progress of experimental investigations of glass dissolution using advanced characterization methods such as atom probe tomography, high-resolution transmission electron microscopy, nano-secondary ion mass spectrometry (nanoSIMS), nuclear magnetic resonance spectroscopy (NMR), sum-frequency generation etc., it is still challenging to study detailed reaction mechanisms, hydrated glass and gel layers structure with nano- and micro-porosity, as well as kinetic and transport behaviors. Atomistic computer simulations can provide detailed mechanistic information to refine our understanding of glass dissolution and shed light on key processes that control dissolution behaviors. Figure 2 shows the multiscale simulation approaches in materials modeling, which consists of methodologies ranging from quantum mechanics, to atomistic/molecular level simulations, to mesoscale and macroscale methods. At the longest time and length scales are continuum simulations that include finite element analysis, fluid dynamics, and reaction rate calculations based on rate theories.

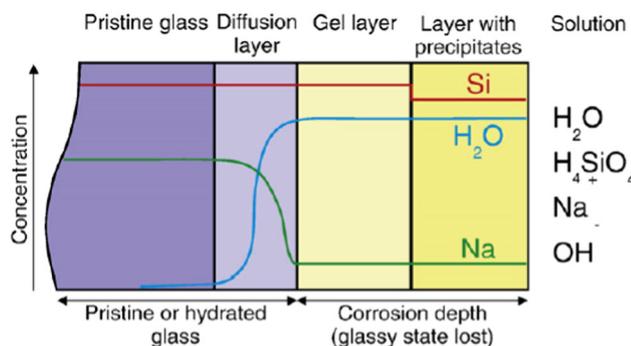
Such higher scale models are extremely valuable, particularly on more applied aspects of research such as predicting the response of glass to long-term geological disposal. For example, Grambow and Müller initially proposed that the dissolution rate of glass is controlled by the level of silica saturation in the solution and can be described by first order rate law on the foundation of chemical reaction affinity of equilibrium thermodynamics and transition state theory.<sup>10,11</sup> Further development resulted in the formation of the GRAAL model (Glass Reactivity with Allowance for the

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**Fig. 1** Regions alteration layer (not to scale) of glass after corrosion (reprinted from ref. 7 Copyright 2010, with permission from Elsevier)

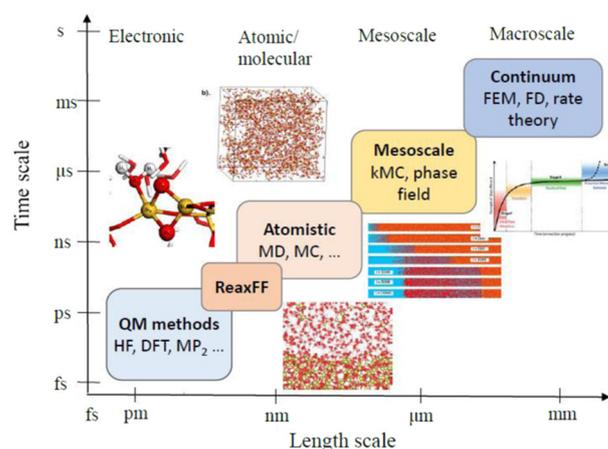
Alteration Layer) of nuclear waste glass dissolution, which include the formation of a passivating reactive interphase (PRI) formed through hydrolysis and condensation in the hydrated gel layer.<sup>3,4,12</sup> The PRI has been identified as a barrier to water transport into the glass and solvated ions into the solution, resulting in transport inhibition effect on glass alteration. While evidence of PRI is limited, Gin et al.<sup>13</sup> used nanoSIMS to identify a dense region 0.5 micron thick between the glass and gel regions, reported to be the first direct evidence of PRI from experiment. While analytical models are critical to developing an understanding of long-term glass dissolution model, atomistic simulations are also extremely powerful in highlighting the reaction mechanisms, structural, and compositional differences, which control dissolution at the small scale and have compounding effects on large scale systems over long time frames.

This review will focus on atomistic scale simulations ranging from electronic, atomistic, and mesoscale methods. In order of decreasing accuracy and increasing computational efficiency, quantum mechanical (QM) simulation methods, classical molecular dynamics (MD) simulations, and kinetic Monte Carlo (KMC) methods have all been extensively applied to understanding the mechanisms and process, which control glass dissolution. Details of these methods, including the advantages, disadvantages, and recent successes in the field of glass dissolution by the use of first-principles (ab initio), classical MD, and KMC simulation methods are discussed in subsequent sections. These include the QM level static transition state first principles simulations to identify the detailed water–glass reactions and fully dynamic simulations using ab initio MD simulations. Furthermore, classical MD simulations using empirical potentials to study multicomponent borosilicate glasses, silica–water interfaces and fully hydrated nanoporous silica structures will be reviewed. Additionally, future challenges and opportunities for simulations to provide added insight into the mechanisms and processes of glass dissolution are included.

### FIRST-PRINCIPLES-BASED SIMULATIONS OF GLASS–WATER INTERACTIONS

Interactions and reactions in the water–silica system

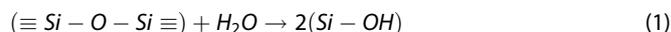
First principles calculations provide the most accurate energies and forces and thus the most reliable reaction pathways and energetics for water–silica interactions. However, due to the high computational cost to solve time independent Schrödinger equation of electrons, approximations must be used. For liquid water and water–solid interactions, density functional theory (DFT) is the mostly widely used approximation. Earlier first principles calculations used cluster models that consists of a small group of atoms with hydrogen saturated dangling bonds to represent a surface or bulk material.<sup>14,15</sup> Due to localized charge transfer, cluster calculations provided reasonable analog to real situations



**Fig. 2** Multiscale simulation methods and applications to water/glass interactions and glass dissolution (reprinted with permission from: ref. 82 copyright 2004, with permission from Elsevier and ref. 98 copyright 2016, with permission from Elsevier; reprinted with permission from ref. 23 copyright John Wiley and Sons 2015, and ref. 2 copyright John Wiley and Sons 2013)

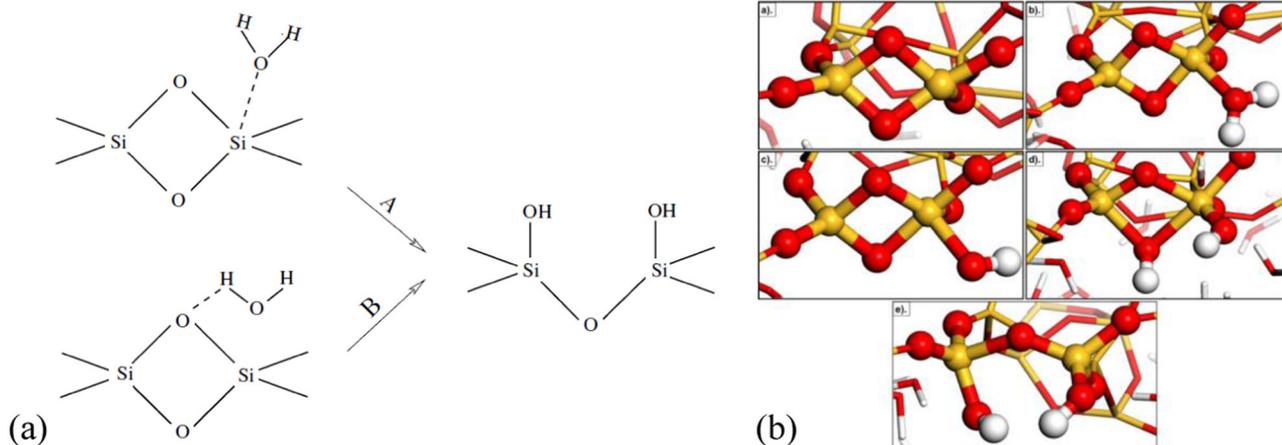
but often constrain surface or bulk effects.<sup>16</sup> Only in recent years has computational efficiency increased to allow for simulation of surfaces and water–solid interfaces.<sup>17</sup> Recent calculations have also considered the effect of pH on the reaction energy barriers to break covalent network former–oxygen–network former linkages.<sup>18,19</sup>

In silicate glass dissolution, silica is the most durable component due to the stable siloxane bonds that form the backbone of the glass network, thus breakage of the Si–O–Si linkages is considered a rate limiting step.<sup>20</sup> DFT-based first principles calculations have been widely used to investigate the reaction mechanisms and energies for hydrolysis of the siloxane bonds (Eq.1).



Due to its high strain energy, two-membered ring (2-Ring) defects, two SiO<sub>4</sub> tetrahedron connected through edge sharing, are often selected for investigation of reaction mechanisms.<sup>14,16,21,22</sup> Two different reaction mechanisms for siloxane bond breakage were proposed by Masini and Bernasconi (Fig. 3).<sup>22</sup> The first involves an oxygen atom in a water molecule creating a short lived pentacoordinated silicon defect (Si<sup>5</sup>), which causes siloxane bond rupture and the transfer of a proton to the non-bridging oxygen formed during bond breakage, forming two silanol groups (outlined in Fig. 3).<sup>23</sup> In the second mechanism, one of the two hydrogen in the water molecule bonds with a bridging oxygen, forming a protonated bridging oxygen, causing siloxane bond breakage and disassociation of the water molecule through formation of two silanol groups. The first reaction, which includes the formation of a Si<sup>5</sup> intermediate defect, has been the most commonly reported. Energy barriers for the breakage of 2-Ring defects are between 0.3–1.27 eV, and vary with simulation method and cluster size.<sup>14,15,22</sup> Differing energetics of the formation of the intermediate defect, either Si<sup>5</sup> or protonated bridging oxygen, are credited with preference for Si<sup>5</sup> reaction mechanism.<sup>22</sup> Silica linkages with defects in the local coordination environment are even more reactive with undercoordinated silicon decreasing the siloxane energy barrier by ~0.3 eV.<sup>15</sup> This work highlighted the variability in the siloxane bond energies, and that selective bond breakage can alter the structure of interfaces and gel structures.

While the above analysis focuses on siloxane bonds in clusters or flat surfaces, surface curvature also can affect both accessibility of defects and the stress state of the surface siloxane bonds.<sup>24</sup> Due



**Fig. 3** **a** Two proposed reaction mechanism of water with two-membered ring defects in silica that lead to breaking of the Si–O–Si bond and defect removal (ref. 22 copyright IOP. Reproduced with Permission. All rights reserved). **b** Reaction mechanism of two-membered ring opening from AIMD simulations (adapted with permission from ref. 99 Copyright 2016 American Chemical Society)

to the development of complex silica gel structures during dissolution, a single bond on a flat surface is not a realistic view of defect sites. For example, removal of 2-Ring defects decrease in nanoporous silica systems where defects are located on complex internal pore surfaces, affecting the reactivity of silica gel.<sup>23</sup> Atomistic simulations are well positioned to investigate the role of surface character on the reactivity of siloxane bonds exposed to the environment. Experimental evidence demonstrates that dissolution develops preferentially at sharp points, smoothing the corners of jagged particles<sup>25</sup> and ledges.<sup>26</sup> Concave surface are more difficult to investigate, but in complex nanoporous silica systems, which include small pore sizes with highly curved internal surfaces, reactivity of 2-Ring defects is much lower.<sup>23</sup> Further investigations of the atomistic scale can highlight surface defects or features are most vulnerable to water attack, which can then inform microstructural engineering of glasses. For example, if small pores are resistant to dissolution, templating glasses with pores may alter the residual dissolution rate. This is just one avenue through which atomistic modeling of glass dissolution can provide unique and valuable insight, which can be incorporated into the development of corrosion resistant glasses.

Activation energies and siloxane bond stability also changes with the coordination of the silicon, which can be investigated in detail by atomistic simulations. Theoretical dissolution begins with a perfectly coordinated  $Q_4$  species, a silicon bonded to four bridging oxygen, and then siloxane bonds break one by one, forming a  $Q_3$ , then a  $Q_2$ , a  $Q_1$ , and finally a  $Q_0$  species ( $\text{SiO}_4\text{H}_x$ ).<sup>12</sup> During each siloxane bond breakage a NBO and a under-coordinated silicon defect will form and are hydroxylated through consumption of water molecules. The energy barrier for different siloxane bond breakages cannot be identified experimentally, but energetics for removal of  $\text{SiO}_4$  units are measured as 0.62–1.12 eV.<sup>26,27</sup> Activation energies vary with solution compositions, temperature, and the use of bulk or powdered samples.<sup>28,29</sup> Energy barriers are lower than the Si–O bond energies of 5–6 eV<sup>30</sup> indicating the important role that water plays in lowering energy barriers. Criscenti et al.<sup>19</sup> attempted to identify a connection between the connectedness of the silicon and stability of related siloxane bonds but did not find a clear relationships, indicating the complexity of the silica dissolution mechanisms. Identifying the changing stability of the siloxane bonds with environment would allow for engineering-specific glass compositions, which contain specific  $Q_n$  ratios to alter dissolution rates. Therefore, detailed high-accuracy investigations of changing bond stability can be an effective method of understanding glass dissolution and working

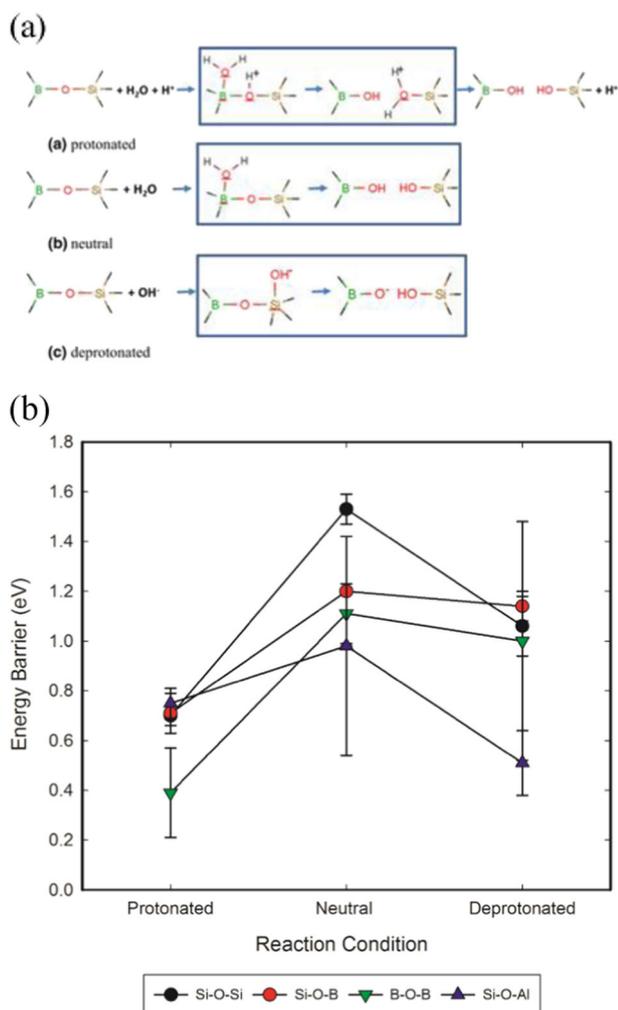
to create unique glass systems, which allow for controlled dissolution.

Interactions and reactions of the water-multicomponent oxide glass systems

Ultimately, nuclear waste glasses are not composed solely of silica, and boron and aluminum are also present as network forming species along with network modifiers, such as alkali and alkali earth oxides.<sup>20</sup> Among the three critical processes of glass dissolution: hydration, hydrolysis, and ion-exchange, hydrolysis is a critical step. In multicomponent glasses, hydrolysis occurs in multiple cation–oxygen–cation linkages with varying energy barriers. The changing stability of M–O–M linkages in glasses is implicated from the creation of the silica rich remnant structure during glass dissolution.<sup>12</sup> Stability of Al–O–Si linkages was performed by Xiao and Lasaga<sup>31,32</sup> and Kubicki,<sup>33,34</sup> and Bouyer<sup>35,36</sup> for investigation of the weathering and hydrolysis of aluminosilicates. Borosilicates are not as well studied, though Lee and Stebbins as well as Tossell and Saggi-Szabo investigated Si–O–B linkage stability in clusters with Zapol et al. extending the analysis to surfaces.<sup>1837,38</sup>

M–O–M linkage stability is affected by the pH of the surrounding fluid, with both protonated and deprotonated systems investigated to approximate acidic or basic conditions. Data compiled in Fig. 4 demonstrates that all linkages exhibit the most stability at neutral conditions, with both protonation and deprotonation affecting the energy barrier. The introduction of a proton results in a decrease in the energy barriers and alters the relative stability of the network formers. Geneste et al.<sup>36</sup> investigated hydronium interactions with Si–O–B linkages identifying and ranked reactivity of types of bonds under protonation conditions, with B–O–B linkages appearing to be the least stable, followed by Si–NBO, and then Si–O–B structures. Protonation effects are also clearly seen in the case of Al–O–Si linkages, with hydroxyls of the Al–O–Si structures by proton absorption onto the bridging oxygen.<sup>35</sup>

Conversely, deprotonation conditions decrease the energy barriers though the effect is not as severe. Identifying the changing mechanisms of water interactions with M–O–M linkages can identify differences in the stability of different M–O bonds, which can be used to predict the response to different glass compositions to the resulting residual rate. Combining activation results for M–O–M linkages with changing coordination environments has indicated which are more or less stable in particular solutions, which can be used to predict glass dissolution under



**Fig. 4** **a** Introduction of the effect of pH on the energy barrier of breaking cation–oxygen–cation linkages (reprinted with permission from ref. 18 copyright John Wiley and Sons 2017). **b** Summary of energy barrier for breakage of network former linkages. Data from refs. 18, 31, 95, 99

changing environments. This demonstrates the power of DFT methods in understanding the role of localized pH and mixed network formers on the stability of multicomponent glasses.

As DFT efficiencies continue to improve it is becoming possible to investigate the surface reactivity of multicomponent glasses with water for larger systems. The majority of this work has been performed by Tilocca and colleagues<sup>39</sup> who investigated the stability of multicomponent bioactive glasses in aqueous environments. Many of the lessons learned and best practices from the investigation of bioactive glasses can be extended, and will provide insight into the role of surfaces on the dissolution behaviors of complex nuclear waste glass compositions.

#### Classical MD simulations of water/glass interactions and dissolution

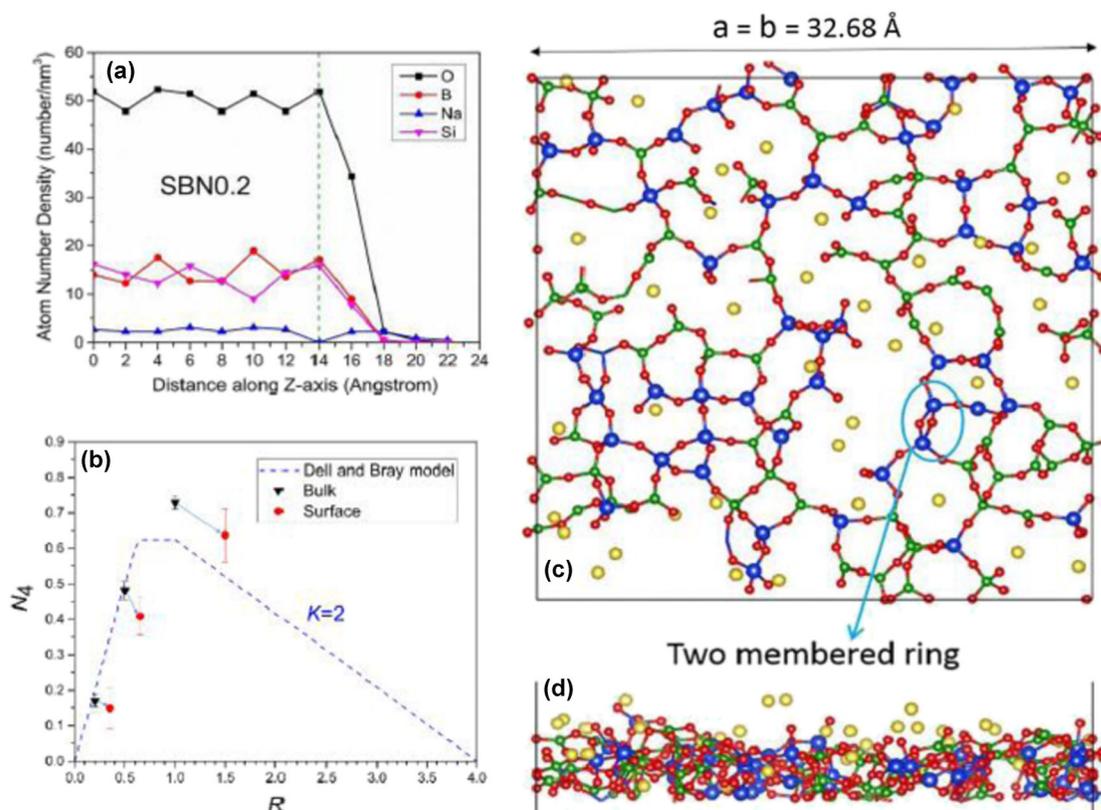
**Forcefield development for multicomponent oxide glasses.** Classical MD employs analytical empirical potentials to describe interatomic interactions resulting in higher computational efficiency and larger system sizes. Classical MD is an attractive option to extend the time and length scale of ab initio simulations (Fig. 1). Classical MD is an effective method to generate atomic structures of glasses, in which larger system sizes and longer time scales

allow for description of medium range structural features in glasses and reaction kinetics. In addition, potentials that enable description of chemical reactions can be used to study water–glass interaction and interfaces, as well as water behaviors in porous glass structures. These two types of simulations: glass structure generation and glass–water interactions represent two common classical MD simulations used to understand glass dissolution.

MD simulations have been extensively applied to study the structure and properties of glasses, which lack long range order and pose significant challenge in experimental investigations. Early potentials of silica include long range Coulombic forces and short range two-body and three-bodied interactions in various forms.<sup>40,41</sup> Potentials were then developed for more complex silica glasses including alkali silicates and aluminosilicate glasses.<sup>42,43</sup> Particularly, D.M. Teter developed a set of empirical potentials for oxides by parametrization to mineral structures and properties.<sup>44</sup> These potentials have been tested in wide range silicate, aluminosilicate, and phosphosilicate glasses with alkali, alkali earth, transition metal, and rare earth oxides by Du and co-workers.<sup>44,45</sup> Pedone et al.<sup>46</sup> developed a set of partial charge potential with the Morse potential form for silicate glasses that include a number of the common alkali, alkali earth, and aluminum oxides. Tilocca also developed a set of full charge potential that included polarization of oxygen ions using the Shell model<sup>47</sup> to model bioactive glasses.

Nevertheless, many of these potentials do not include parameters of boron oxide due to the composition dependent coordination change of boron. However, boron oxide is commonly included in nuclear waste glasses due to its capability to lower the melting temperature and viscosity of the melt. Hence, modeling multicomponent nuclear waste glasses is particularly challenging. Some potentials exist for alkali borates but only a few for borosilicate glasses. Recently, Kieu et al.<sup>48</sup> developed a set of two-body potential with composition dependent parameters for atomic charges and B–O interaction parameters by fitting to the boron coordination change from Dell and Bray model based on NMR studies. The Kieu potential was able to describe changing boron coordination with composition. Deng and Du tested wide composition range of the validity of the Kieu potential<sup>49</sup> and extended the potential to include alumina.<sup>49</sup> These potentials have been used to study the surface structure of sodium borosilicate glasses (Fig. 5). It can be seen that the boron coordination of the bulk glass agree well with the Dell and Bray model.<sup>50</sup> The glass surface has shown an enrichment of sodium and compositional changes as compared to the bulk.<sup>51</sup> Therefore, the glass surfaces show different chemistry and structure from the bulk, features which were also observed by Criscenti et al.<sup>19</sup> in MD simulations of sodium borosilicate glass surfaces.

Investigation of the changing coordination of boron in the multicomponent glasses used for nuclear waste disposal can serve as a representative study of how classical MD investigations can provide unique insight into glass structure. With recently developed potentials by Deng and Du,<sup>49</sup> sodium boroaluminosilicate glasses that represented simplified version of the International Simple Glass (ISG), a model glass developed by the international community to understand physical and corrosion behaviors of nuclear waste glasses, were studied using MD simulations through the simulated melt and quench process (Fig. 6 shows the snapshot of the final simulated glass structure). It can be seen that these glass former oxygen polyhedrons consisting of  $[\text{SiO}_4]$ ,  $[\text{AlO}_4]$ ,  $[\text{BO}_3]$ , and  $[\text{BO}_4]$  connect together through bridging oxygen to form a three dimensional network. The cation oxygen pair distribution functions identify Si–O, Al–O, and Na–O bond distances of 1.61 Å, 1.73 Å, and 2.50 Å, respectively (Fig. 7a). The B–O pair distribution (Fig. 7b) shows an average B–O bond distance of 1.47 Å with a shoulder due to shorter B–O bond distances in threefold coordinated boron ( $^3\text{B}$ ). From the



**Fig. 5** Sodium borosilicate glass from MD simulations.<sup>51</sup> Surface composition profile **a** and boron  $N^4$  as a function of  $R$  (soda to boron oxide ratio) for the bulk and surface **b**. Surface structure of sodium borosilicate glasses: top view **(c)** and side view of top 5 Å **(d)** (reprinted with permission from ref. 51 copyright John Wiley and Sons 2017)

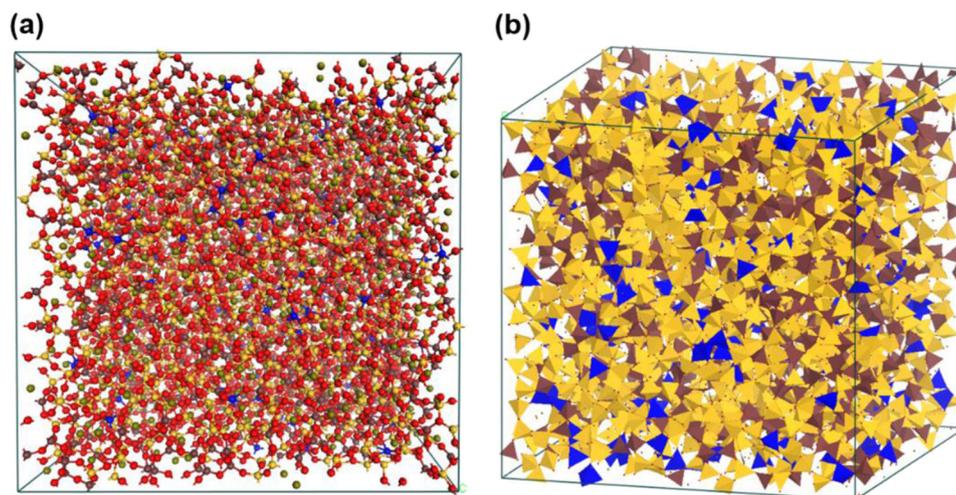
deconvolution, the percentage of fourfold coordinated boron ( $^4B$ ) can also be determined to be around 80%. Thus, in the ISG composition, majority of boron is in fourfold coordination state. With carefully developed and validated potentials, the complex structures of the mixed glass former nuclear waste glasses can be generated with structure features in good agreement with experimental data. These structures can provide a foundation of other studies such as radiation effects, diffusion behaviors, surface, and surface reactions. After the successful development of multicomponent glass model, the role of structural changes of the glass on dissolution rates can be further established so that glass dissolution can be predicted on geological time scales.

**Forcefield development for the water–silica systems.** Including water–silica interactions into classical MD forcefields is critical in allowing for the atomistic simulation of glass dissolution on a larger scale. Many attempts have been made to develop such a forcefield, including Feuston and Garofalini, who performed water–silica simulations using a dissociative water–silica potential in the early 1990s.<sup>52</sup> Recently, Mahadevan and Garofalini developed a dissociative water–silica forcefield based on water potentials by Guillot and Guissani.<sup>53</sup> Another forcefield used the BKS potential for silica and a SPC/E water model with Buckingham interactions for water–silica interfaces was developed by Hassanali and Singer.<sup>54</sup> Other water–silica potentials have been developed,<sup>55,56</sup> however, truly reactive potentials that can describe silica and water structures, reaction pathways, and energetics are rare.

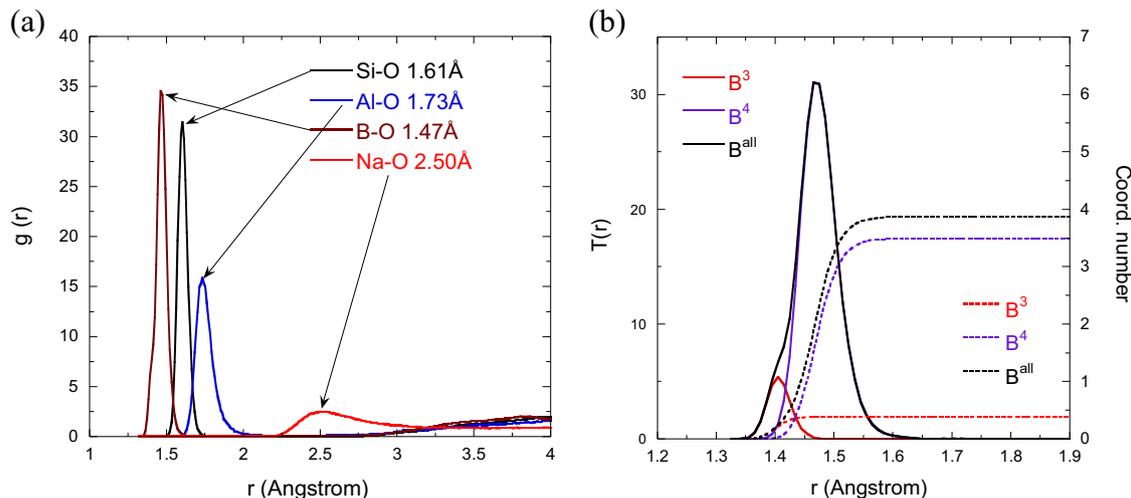
One forcefield that includes water–silica reactions is a bond order based reactive force field (ReaxFF) with dynamic charge equilibration developed by Goddard, van Duin, and coworkers.<sup>57</sup>

ReaxFF includes indistinguishable atomic species, thus oxygen atoms in water and oxygen in silica are of the same species, and atoms smoothly transition from one chemical species to another.<sup>58</sup> Additionally, charges in the systems are not fixed, but vary depending on local geometry and chemical environment. ReaxFF was first parameterized for water–silica systems in 2010 by Fogarty et al.<sup>58</sup> then readjusted by Yeon and van Duin to provide greater accuracy in water–silica reaction energy barriers.<sup>59</sup> Rimsza et al. used DFT-based ab initio MD simulations of water–nanoporous silica interactions to validate two versions of ReaxFF potentials for water–silica interactions.<sup>60</sup> It was shown that the new refined model (ReaxFF-2015) can describe the reaction energy barrier of Si–O–Si breakage (hydrolysis reaction) much better than the 2010 version (Fig. 8a). Also, the comparison shows the reactivity is different between the two versions of the parameters as shown in the concentration of the 2-Ring defects (Fig. 8b). Overall, the two ReaxFF potentials were able to describe the water–silica interfacial structure well but could improve the description of the water–silica reaction energetics and kinetics.

The ReaxFF has been used to identify the reactivity of the silica-gel formed during glass dissolution through interfacial gel models developed by Rimsza and Du.<sup>61</sup> By inserting a silica-gel structure between dense silica and bulk water, the dissolution of the silica from the gel to the water regions can be monitored.<sup>61</sup> Results found the removal of low coordinated silica out of the gel, resulting in an increased connectivity of the remaining gel structure, as well as the development of high silica concentrations adjacent to the water–gel interfaces.<sup>61</sup> Such simulations can be extremely powerful in identifying the evolution of changes of the interface during glass dissolution, and provide information on how the composition and structure of the gel affects the residual



**Fig. 6** Snapshot of ISG glass structure from MD simulations. **a** Ball and stick representation: red: oxygen, orange: silicon, blue: aluminum, brown: boron, green: sodium. **b** polyhedron representation. Yellow tetrahedron:  $\text{SiO}_4$ , blue tetrahedron:  $\text{AlO}_4$ , brown triangle and tetrahedron:  $\text{BO}_3$  and  $\text{BO}_4$



**Fig. 7** **a** Pair distribution functions (PDF) of cation–oxygen pairs **b** deconvoluted boron–oxygen total correlation function and accumulated boron coordination number of ISG glass

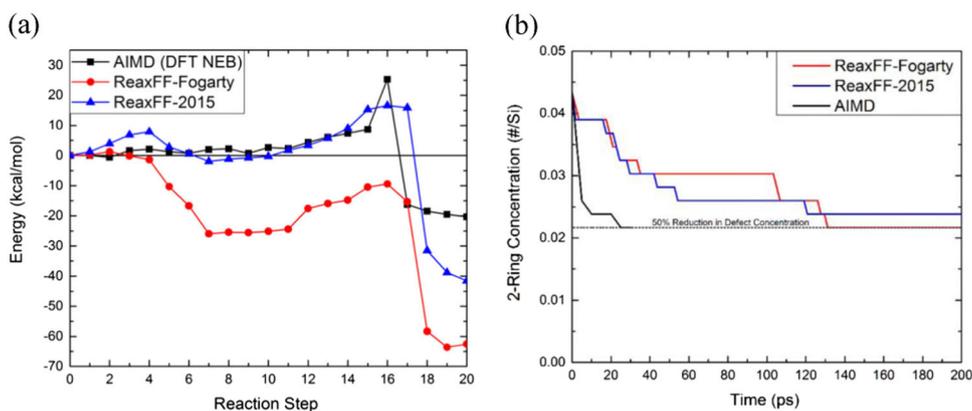
dissolution rate. Expansion of this work into multicomponent systems would allow for the identification of the role of different network modifiers and formers can glass dissolution.

**MD simulations of water–silica interactions.** By using the above-mentioned forcefields, the water–silica interactions and reactions have been studied using classical MD simulations. Garofalini and co-authors performed some of the early MD simulations of water–silica glass interactions. They analyzed the structure and hydroxylation of silica surfaces<sup>62</sup> as well as silica polymerization.<sup>63</sup> With advances in potential development the role of the original defective surface in forming silanol concentrations were identified.<sup>54,56,64</sup> Classical MD simulations have also been able to reproduce both of the silica–water reaction mechanisms found in ab initio simulations<sup>65,66</sup> due to the inclusion of DFT reaction pathways and energies.<sup>59</sup> Classical MD simulations tend to favor siloxane bond breakage by absorption of a proton onto a bridging oxygen site, noted by Lockwood and Garofalini<sup>65</sup> and Rimsza, van Duin, and Du.<sup>66</sup>

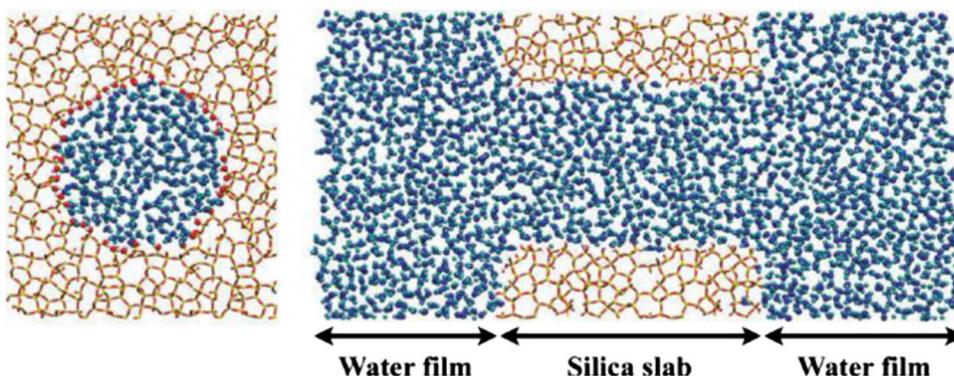
Later simulations looked into the gradual dissolution of silica glasses. Dissociation energy barriers of different  $\text{Si } Q_n$  species

(silicon oxygen tetrahedron with  $n$  bridging oxygen) on silica glass surfaces were investigated using the potential mean force approach with MD simulations. By using the dissociative water–silica potential developed by Mahadevan and Garofalini,<sup>53</sup> it was found that among the four ( $Q_4 \rightarrow Q_3$ ,  $Q_3 \rightarrow Q_2$ ,  $Q_2 \rightarrow Q_1$ , or  $Q_1 \rightarrow Q_0$ ) reactions, the  $Q_3 \rightarrow Q_2$  and  $Q_2 \rightarrow Q_1$  reactions have the highest activation energy of  $\sim 14.1$  kcal/mol, and is the rate limiting step in bulk silica dissolution.<sup>19,24</sup> These barriers are in the lower range of the experimental energy barriers of 14–24 kcal/mol and below values from cluster-based ab initio calculations (18–39 kcal/mol).<sup>19,24</sup> Similar differences in energy barriers for siloxane bond breakage were identified by Du and de Leeuw on quartz surfaces.<sup>57</sup> Understanding how the local environment alters stability of siloxane bonds is critical to understanding how silica dissolves. If certain conditions/environments leads to increased stability, that is a structural or compositional feature, which can be targeted in the development of nuclear waste glasses.

In addition to investigating activation energies, classical MD simulations have been used to study other aspects of the water–silica interface. For example, structured water has been identified adjacent to the silica interface and extends 10 Å into the



**Fig. 8** **a** Comparison of reaction energy vs. reaction coordinates for ab initio and classical molecular dynamics with two versions of the ReaxFF forcefield. **b** Concentration of two-membered ring defects as a function of simulation time (**a**, **b** reproduced with permission from ref. 99 Copyright 2016 American Chemical Society)



**Fig. 9** MD simulations of water in cylinder pores of silica glass. Cross section views along the pore and perpendicular to the pore. The silica pore diameter is 4 nm. (reproduced with permission from ref. 70 Copyright 2012 American Chemical Society)

water.<sup>68</sup> Structured water experiences localized layering as well as the development of hydrogen bond networks and sharp decreases in the water self-diffusivity.<sup>69,70</sup> Figure 9 shows the cross section views of MD simulations of water in cylinder pores in silica from MD simulations. The structure and properties of water depend on the pore diameter with nanoconfinement in pores smaller than 1 nm. For pores with larger diameters (2 to 4 nm), water in the center of the pore behaves like bulk water. The simulation results show that the first monolayer water on silica surface is immobile while the rest of the water freely diffuses. The formation of structured water and limited atomic movement through water–silica systems impacts silica reactivity. It has been suggested that structured or nano-confined water inside the silica gel can influence water and ion transport during dissolution. With narrow pore structures, silica gel can limit the water diffusion and thus controls the speed of dissolution. Further investigation of the effect of nanonconfinement in more complex structures would identify if this effect could be scaled up to allow for passivation of surface layers due to limited water kinetics.

Aspects of water and silica interdiffusion have also been investigated, including details of hydronium ion formation in water as an intermediate step in fast proton transport.<sup>71</sup> Due to the ability to disassociate the water molecule, penetration of the water into the glass up to 8 Å away from the interface has been observed using multiple classical MD potentials.<sup>58,72</sup> This indicates the importance of a dissociative potential to allow for the possibility of water molecules breaking and recombining either inside or outside the silica structure. On the opposite end, the diffusion of silica monomers into water has also been investigated, to provide insight into whether nucleation of silica on the surface

may cause reorganization of silica–water interface. Simulation of  $\alpha$ -quartz indicates that the surface attracts the  $\text{SiO}_4\text{H}_4$  with little change in the surface structure after reattachment of the tetrahedron resulting in a more stable quartz surface.<sup>67</sup> Attraction of the silica monomer to the surface may account for the growth of the protective layer and the low concentration of silica far from the interface.

Hydrated porous gel structures have also been investigated in the cement community where structured water molecules distributed in calcium silicate hydrate (C-S-H) determine the mechanical behavior. For example, Hou et al.<sup>73</sup> studied the C-S-H gels with different water contents and their mechanical behaviors using the CSHFF potential. It was found that the increase of water content transforms C-S-H gel into a layered structure. Hou et al.<sup>74</sup> also studied the water confinement in nanoporous C-S-H gel using the ReaxFF potential. It was found that the calcium silicate skeleton significantly influence the adsorption, reactivity, hydrogen-bond network and diffusivity of water molecules. Colliding of water molecules with the calcium silicate backbone was found to weaken the stability of the gel. Despite different chemistry and applications, the porous gel structure in C-S-H and confined water behavior and reactivity show similarity to the gel layer formed during glass dissolution. Plenty of experimental data is available to validate these models and some understanding can be borrowed in the glass corrosion field.

Overall classical MD simulations have provided detailed atomic level information on mechanisms and processes in glass dissolution, but further investigations of combined effects, has been limited. Additionally, the accessible time scale of MD is determined by the time step that is required to be small enough

to ensure accuracy of integration of equation of state. This limits most practical simulation scale to nano to micro-seconds. To extend the simulation time other methods need to be used.

#### Monte Carlo simulations of glass dissolution

Monte Carlo (MC) is a stochastic method that is commonly used to obtain numerical solutions of complex processes where analytical solutions are difficult to calculate. Application of MC methods to glass dissolution involve solving coupled hydrolysis/dissolution and condensation reactions.<sup>3,75</sup> MC simulations which include a time component are term kinetic MC (KMC). KMC evolves the system from state to state based on reaction rates and can enable simulations of infrequent events and process longer time scales compared to MD simulations.<sup>76,77</sup>

Aertsens and coworkers pioneered KMC simulations of glass dissolution of alkali silicate glasses,<sup>75,78,79</sup> where the glass structures were approximated by diamond lattices due to the topological similarity between the lattice and the network structures in silica. Two types of lattice sites, one easily dissolving and one slowly dissolving component represented by silicon and sodium, respectively, were randomly distributed on the lattice sites. When modifier concentration was high, the dissolution was found to be stoichiometric and there was no gel layer formation. With increased glass former concentration the dissolution became non-stoichiometric and a stable surface layer formed.<sup>79</sup> In additional MC simulations of glass dissolution, it was found that a protective gel layer formed due to silica adsorption or precipitation from the solution. The dissolution rate from MC simulations was found to obey the first order rate law, in agreement with the experimental data.<sup>78</sup>

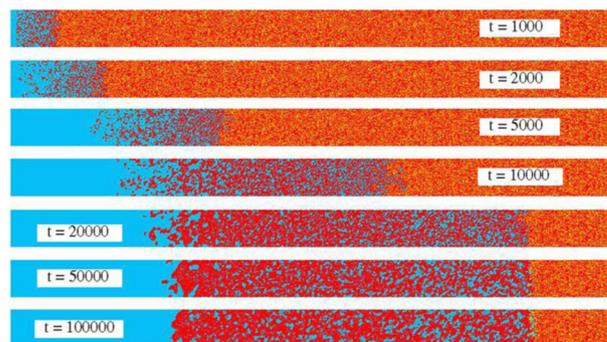
Devreux et al.<sup>80</sup> further developed the MC methodology and applied it to study the dissolution of sodium borosilicate glasses.<sup>81</sup> Simulations were performed on a diamond lattice with silicon and boron atoms randomly put on the vertices and their proportion consistent to the glass composition, while sodium atoms were put into the interstitial sites near silicon or boron. Silica dissolution is described by three rate constants corresponding to silica with one, two, or three bridging oxygen. The dissolution-condensation equilibrium is schematically expressed as,



where the  $Q_n$  denotes silicon atoms with  $n$  siloxane bonds (or  $n$  bridging oxygen) and  $Q_0$  is silicic acid ( $\text{Si}(\text{OH})_4$ ). And the dissolution to condensation rate constant ratio  $w_n/w_c$  is expressed as

$$\frac{w_n}{w_c} = \exp \left[ -\frac{\Delta H_n}{K_B T} \right] \quad (3)$$

where  $\Delta H_n$  is the reaction enthalpy, which can be derived from QM calculations or fitted to reproduce experimental data, and  $K_B$  is Boltzmann constant and  $T$  is the temperature.<sup>82</sup> The MC simulations were performed in two phases: the dissolution and the condensation phase,<sup>82,83</sup> while more complex algorithms were adopted in more recent MC simulations.<sup>84</sup> In the dissolution phase, the surface grids were scanned and the soluble species such as sodium and boron were dissolved unconditionally while the silicon  $Q_n$  species were dissolved based on the probability  $w_n$ . The dissolved species were replaced with water. In the condensation phase, silicon atoms were deposited at random positions according to the rate of  $w_c \times c_{\text{Si}}$ , where  $c_{\text{Si}}$  was the silicon concentration. This process generated porous silica at the water-glass interface due to removal of soluble species such as boron and sodium, the removal of isolated silicon species, and the adsorption or redeposition of silicon.<sup>82</sup> The model was able to reproduce the experimental thickness of dissolution alteration layer for samples with different surface area to volume ratios. Figure 10 shows the gel layer formation and morphology



**Fig. 10** Evolution of the gel layer morphology during dissolution of borosilicate glasses from MC simulations. Silicon: red pixels, boron: yellow, sodium: not shown, water: blue (reprinted from ref. 82 Copyright 2004, with permission from Elsevier)

evolution as a function of dissolution time from MC simulations of dissolution of a sodium borosilicate glass.<sup>85</sup> It shows that the gel layer is free of boron and sodium and consists of silica with silicon density similar to the bulk glass. Also, the gel structure appears to be inhomogeneous with higher porosity at the gel/glass interface than the gel/water interface.

An important aspect that has been overlooked or treated too simply in early MC simulations of glass dissolution is the transport of dissolved silicon species through the altered layers. Kerisit et al.<sup>84</sup> systematically studied three diffusion models in MC simulations of sodium borosilicate glasses and evaluated the simulation results by comparing with experiments. The three diffusion models include the instantaneous homogenization model which represents the limiting case of much faster diffusion of silicon species as compared to the rates of hydrolysis and condensation, the model with linear silicon concentration across the altered layer, which has been used earlier by Ledieu et al.<sup>86</sup> and the model coupling of hydrolysis and condensation reaction with the 1-dimensional diffusion model by solving the Fick's second law using a finite different method. Due to the incorporation of diffusion, a more complex six steps MC algorithm were used: dissolution evaluation and execution, glass connectivity evaluation, diffusion, condensation, liquid connectivity evaluation, and the coordination evaluation.<sup>84</sup> The results show that the instantaneous homogenization and linear diffusion model are appropriate for glasses that dissolves rapidly, for example, sodium borosilicate glasses with low silica content and those with low zirconia concentrations. But for the less dissolvable glasses with higher silica content such as SON68, the assumption of linear diffusion became problematic as silica concentration in the altered layer is not linear, but changes significantly with time and decreases in magnitude with respect to the bulk solution. This highlights the importance of explicit treatment of diffusion of dissolved species in the altered layer in MC algorithms for glass dissolution simulations.<sup>84</sup>

Using similar approaches, Ledieu et al.<sup>87</sup> studied the effect of alumina and zirconia in the dissolution of borosilicate glasses using MC simulations. Two competing processes were found to control the glass dissolution rate: dissolution of soluble components such as B and Na and restructuring of the altered layer due to hydrolysis/condensation reversible reactions. It was also shown that the formation of surface hydrated layer is responsible for slowing dissolution. The replacement of silica with less soluble oxides such as zirconia led to an initial increase of the leached layer thickness, hence a decreased dissolution rate, while further substitution at high zirconia content decreased the leached layer thickness and thus a greater boron release, in agreement with experimental results.<sup>87</sup> This was explained by the fact that these

insoluble oxides impeded the formation of the surface silica layer that controls the dissolution.<sup>87</sup>

Cailleteau et al. also found that the slowdown of the dissolution rate of less durable silicate glasses over time was due to pore closure near the outer surface of the alteration by combining MC simulations with experimental investigations.<sup>88</sup> This kind of morphology transformation provides interpretation of dissolution rate slowdown in some glasses that is different from the theory that accounted for decreasing dissolution rates was to saturation of silica content in the solution, showing that MC can provide insights to complicated processes of dissolution that requires access to long time scales.<sup>88</sup> MC simulations were able to show the formation of the dense polymerized outer layer during borosilicate glass dissolution, nevertheless none of these simulations were able to reproduce the formation of the porous silica gel structure on the top of the dense outer layer, which has been observed experimentally.<sup>84</sup> Fully dense outer layer that prevented diffusion contradicts with experimental observations that there exists a residual dissolution rate in borosilicate glasses, hence further development of MC algorithm to enable the formation of thick gel layer on the top of the dense silica layer is needed.<sup>84</sup> Most of the MC simulations uses regular diamond or cubic lattices with glass network structures mapped on the lattices and modifier cations putting into the interstitial sites. Realistic glass structure models of multicomponent borosilicate glasses can be generated from MD simulations with recently developed potentials.<sup>45,48,49</sup> Another development of MC simulations is thus to incorporate the structure models from MD in MC simulations instead using the ideal lattices.<sup>76,84</sup>

Kerisit et al.<sup>89,90</sup> have further developed the MC simulation methodology for glass dissolutions to take into consideration glass structure features such as NBO and corrosion conditions such as dynamic flow-through experiments.<sup>3</sup> In simulations of flow-through corrosion of borosilicate glasses, it was found that at high flow rate conditions, thick alteration layer was formed and glass dissolves congruently. At low flow rates, highly incongruent dissolution was observed with formation of a permanent protective layer similar to static dissolution conditions. This protective layer, however, can be disrupted or prevented at even slow flow rate that led to intermediate resumption of glass corrosion. Kerisit et al. also studied the effect of glass composition such as the addition of alumina to borosilicate glasses on glass corrosion at static conditions.<sup>90</sup> The role of alumina was found to be complicated. Alumina decreases corrosion due to stronger Al–O–Si linkage than Si–O–Si linkages. On the other hand, alumina has opposite effect on the protective layer formation that controls the residual rate of glass dissolution. Alumina slows down the hydrolysis-condensation reaction of silica hence delays the formation of the protective gel layer but it strengthens the glass network and increases its lifetime, which facilitates the formation of the protective layer. As a result, the extent of dissolution (represented by boron leaching thickness) shows a maximum with alumina concentration in zirconia containing boroaluminosilicate glasses, in agreement with experiments.<sup>90</sup> These results show that MC can provide mechanistic understanding of glass dissolution and glass-water interfacial reactions. It can also be used to study the effects of glass composition and testing conditions thus glass dissolution behaviors.

#### Current challenges and opportunities

During glass dissolution, several different interfacial layers are formed between the pristine glass and the bulk solution. The atomic and microstructure of these interfacial layers are responsible for controlling the residual rate. Multiple competing mechanisms may occur and increase complexity of the analysis.<sup>12</sup> The structure and properties of the interfacial gel layers are thus critical to identifying the residual rate of glass dissolution.<sup>12</sup>

Computational tools provide the opportunity to investigate the silica gel alteration layers and isolate specific reactions in order to identify which of the competing mechanisms dominates the dissolution process. Currently, *ab initio* and classical MD simulations have investigated the hydrolysis phase of dissolution but condensation or polymerization of silicic acid to form the gel and protective layer could not be studied due to the long simulation times necessary for the reaction kinetics. Traditionally, MC methods have been used to investigate this regime, though with increasing computing power and the development of reactive potentials, these processes might be able to be studied with MD as well.

Nuclear waste glasses are complicated multicomponent oxides, and much of the dissolution phenomenon varies with composition. For example, inter diffusion occurs between the network modifiers in the glass with the aqueous environment, and changing stability of network formers is credited with the formation of the silica rich gel layers. Thus far, the majority of the investigation of glass dissolution using classical MD and *ab initio* methods has focused on the analysis of simpler water–silica systems, selected due to the availability of potentials and the wide interest in silicates. The limited information available on multicomponent amorphous oxides is a detriment to the understanding of glass dissolution, when competing mechanisms require simulation of mobile species in the glass. As the field of glass dissolution continues to mature, focus will need to shift on the role of second and tertiary components. In the use of *ab initio* or DFT methods careful selection of structures due to the small simulation sizes will be necessary, as well as targeted studies to investigate specific aspects of dissolution, such as structural stability of surface features. With classical MD methods the primary challenge is the development of potentials, which are robust enough to handle the chemistry of the complex multicomponent oxides combined with water reactivity.<sup>44,49</sup> While several potentials are currently in development, further detailed validation will be required before the investigation of nuclear waste dissolution.

Most of the MC simulations used ideal diamond or cubic lattices to simplify the simulations and to allow access to larger systems and longer time scales. These lattices are too simplified to represent the complexity of the structure of multicomponent glasses.<sup>75,76</sup> Medium range ring structures, composition dependent coordination change, or the clustering of modifier ions<sup>91</sup> can be important in the dissolution of glasses. The major challenges facing current MC or KMC simulations of glass dissolution is how to include more realistic glass structure information and still keep the computational cost manageable. Thus, applying realistic glass structure models from MD simulations of multicomponent nuclear waste glasses in MC simulations would be a future direction of MC simulations. It has been proposed that other simulation methods such as neural network and genetic algorithm can be used to tackle the challenges of complex glass structures in these simulation processes.<sup>75</sup>

The reaction energy barriers or reaction rate used in MC simulations were usually predetermined in two ways: either from minimum energy path and transition state search based on QM calculations or from fitting the rate constants to reproduce experimental data. When realistic glass structure is used in the MC simulations, it might be possible calculate the reaction rates on the fly during the simulations due to many more possibilities of combination of reactants states in the glass environments during the dissolution process. In this way, the reaction rates can be determined by using effective transition state algorithms such as the dimer method<sup>92,93</sup> according to the local environments during dissolution reactions. This will provide most accurate reaction energies or reaction rates to move MC simulations that will generate most accurate simulations but the challenge is how to keep the computational cost manageable.<sup>76</sup>

**Table 1.** Reaction energy barrier for silica–water cluster calculations through ab initio simulation

Geometry	Energy (eV)	Intermediate defect	Ref.
Two-membered ring (2-Ring) defects	1.08–1.27	Si <sup>5</sup>	14
	0.71–1.11	Si <sup>5</sup>	15
	1.1	Si <sup>5</sup>	22
	0.3	Protonated bridging oxygen	
	0.9	Si <sup>5</sup>	21
	1.17	Si <sup>5</sup>	94
	1.09	Si <sup>5</sup>	66
Unstrained Si–O–Si	1.24	Protonated bridging oxygen	19
	1.65–1.52	Si <sup>5</sup>	95
	1.68	Si <sup>5</sup>	85
	0.86–1.24	Si <sup>5</sup>	96, 97

With ever increasing computing powers and new development of simulation algorithms, these issues and challenges can be addressed and realistic modeling of the long time dissolution behavior of glasses can be achieved.

## SUMMARY

Atomistic computer simulation methods ranging from first principles calculations, ab initio molecular dynamics simulations (AIMD), classical molecular dynamics (MD) simulations and kinetic Monte Carlo (KMC) simulations and their applications to understand glass/water interaction and glass dissolution are reviewed in this paper. It is shown that these simulations provide mechanistic understanding of the strongly coupled ion-exchange, hydrolysis, hydration and associated interfacial processes and transport behaviors during glass dissolution. These simulations also provide insights to the bulk and surface structures of multicomponent glasses, water/glass reaction energetics, porous gel layer formation and water diffusion in confined pores, as well as microstructure evolution due to hydrolysis and condensation of the network structures, which will help to understand the mechanism behind key processes such as the residual rate of glass dissolution. The challenges of the simulations including the development of fully reactive potentials for multicomponent glass–water systems and KMC simulations based on realistic glass structures are discussed. With further development along these and other directions, together with ever increasing computing power and availability of accurate experimental characterizations to validate simulation results, it is conceivable atomistic simulations will play an even more important role in the understanding of long-term glass dissolution behaviors Table 1.

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## AUTHOR CONTRIBUTIONS

J.D. designed the outline of the article. J.M.R. wrote section "First-principles-based simulations of glass–water interactions", J.D. wrote section "Monte Carlo simulations of glass dissolution". Both J.D. and J.M.R. wrote the remaining portions of the manuscript.

## ADDITIONAL INFORMATION

**Competing interests:** The authors declare that they have no competing financial interests.

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