Short- and medium-range structure of multicomponent bioactive glasses and melts: An assessment of the performances of shell-model and rigid-ion potentials

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Classical and \textit{ab initio} molecular dynamics (MD) simulations have been carried out to investigate the effect of a different treatment of interatomic forces in modeling the structural properties of multicomponent glasses and melts. The simulated system is a soda-lime phosphosilicate composition with bioactive properties. Because the bioactivity of these materials depends on their medium-range structural features, such as the network connectivity and the $Q^n$ distribution (where $Q^n$ is a tetrahedral species bonded to $n$ bridging oxygens) of silicon and phosphorus network formers, it is essential to assess whether, and up to what extent, classical potentials can reproduce these properties. The results indicate that the inclusion of the oxide ion polarization through a shell-model (SM) approach provides a more accurate representation of the medium-range structure compared to rigid-ion (RI) potentials. Insight into the causes of these improvements has been obtained by comparing the melt-and-quench transformation of a small sample of the same system, modeled using Car–Parrinello MD (CPMD), to the classical MD runs with SM and RI potentials. Both classical potentials show some limitations in reproducing the highly distorted structure of the melt denoted by the CPMD runs; however, the inclusion of polarization in the SM potential results in a better and qualitatively correct dynamical balance between the interconversion of $Q^n$ species during the cooling of the melt. This effect seems to reflect the slower decay of the fraction of structural defects during the cooling with the SM potential. Because these transient defects have a central role in mediating the $Q^n$ transformations, as previously proposed and confirmed by the current simulations, their presence in the melt is essential to produce an accurate final distribution of $Q^n$ species in the glass.

\section{I. INTRODUCTION}

The special bioactive properties of some surface-active phosphosilicate glasses depend on the presence of large amounts of sodium and calcium modifier cations, whose charge balance is achieved by breaking Si–O–Si bridges and creating a corresponding high concentration of nonbridging oxygen (NBO) atoms, and thus a significant fragmentation of the silicate network. \cite{1, 3} Indeed, experimental and simulation data show that the bulk structure of common, melt-derived bioactive glasses, \cite{1–3} exploited in many clinical applications of implants made or derived from $\text{Na}_2\text{O}:\text{CaO}:\text{SiO}_2:\text{P}_2\text{O}_5$ bioactive glasses, \cite{4–6} the partial dissolution of this highly fragmented structure in a physiological (aqueous) environment is thus relatively fast and leads to a series of reaction steps at the glass surface, which ends with the formation of a strong interfacial bond between the glass and living tissues, such as bone or muscle. \cite{5} This unique tissue-bonding ability is exploited in many clinical applications of implants made or derived from $\text{Na}_2\text{O}:\text{CaO}:\text{SiO}_2:\text{P}_2\text{O}_5$ bioactive glasses, \cite{4, 5} which therefore represent a key reference in the field of biomaterials. \cite{1, 3} Even though significant scientific and technological advances have been achieved since their discovery in the early 1970s, investigations on the atomistic structure of bioactive glasses have only started to appear very recently, despite the obvious importance of these highly detailed data to improve our understanding of their properties. The disordered and multicomponent nature of bioglass systems represents a challenge to experimental and computational approaches to unveil their structure. For instance, while binary glasses have often been modeled using classical molecular dynamics (MD) simulations, \cite{9–13} not as many studies have focused on amorphous oxides containing three or four base components, and in particular bioactive glasses have been seldom modeled by MD. \cite{5–7} The complex nature of bioactive glasses complicates the use of standard MD force fields commonly used for ionic oxides. Si–O and P–O bonds show a mixture of covalent and ionic character, whose specific balance depends on the local coordination environment, such as the concentration and geometry of Na/Ca cations surrounding the individual SiO$_4$ or PO$_4$ tetrahedra or the local intertetrahedral connectivity. Therefore, in principle, the interaction terms of an accurate force field to model multicomponent amorphous silicates should take into account the specific environment surrounding each ion and especially the highly polarizable oxide ions. \cite{14, 15} An implicit,
mean-field inclusion of polarization as in rigid-ion (RI) models using fixed partial charges may not fully reproduce the diverse, often distorted arrangements of silicate and phosphate bonding environments in disordered biomaterials, neither can it account for the dynamical fluctuations in the charge distributions resulting from even small rearrangements in these coordination environments. On the other hand, the explicit inclusion of electronic polarization enables the model to respond to local electric field fluctuations brought about by the ionic motion, as shown by the success of shell-model (SM) approaches to model a large variety of condensed-phase systems, ranging from ionic solids and liquids and their interfaces, to aqueous solutions, and should then yield a more flexible and accurate representation of the structure of bioactive glasses. Some indications in this sense came from our previous SM investigations of binary and ternary silicate glasses, for which the explicit inclusion of the ionic charge polarizability improved the intertetrahedral structure, compared to an RI potential. Following these indications, we recently developed and applied an SM potential to model bioactive glasses. Even though these studies confirm the general suitability of a SM approach to model bioactive compositions, several important issues remain open. The dissolution and bioactivity of these glasses are closely linked to their structure in the medium range; for instance, the network connectivity reflects the structural arrangement beyond the short range and shows interesting correlations with the glass bioactivity. As \textit{ab initio} models of medium-range structural properties would require too large computational resources, it is essential to thoroughly assess the performance of empirical potentials from this perspective. To this purpose, in this work, we compare the structure of large samples of 45S5® bioactive glass obtained using classical MD with SM and RI potentials, and highlight the advantages of an SM approach in reproducing the key structural features of the glass, such as the \(Q^n\) distributions of Si and P network formers. The \(Q^n\) distribution is a convenient measure of the ability of a potential to describe the medium-range structure of the 45S5 Bioglass®, both because it reflects the glass network connectivity and because of the availability of NMR and Raman spectroscopy data, which can be used as direct reference.

Thereafter, we examine the possible effects that determine the better performance of the SM approach by focusing on the glass formation process from the melt. Because of the lack of experimental data on these effects, the corresponding reference data are obtained from Car–Parrinello (CP) \textit{ab initio} MD simulations of a smaller sample, whose structural evolution during the melt-and-quench process is compared to the results of classical MD simulations using the SM and RI potentials. This detailed comparison on two different scales allows us to highlight specific features in the short and medium ranges whose accurate description needs an explicit treatment of polarization. From a different perspective, the present calculations provide new insight into whether and up to what extent polarization effects influence the structural properties of complex amorphous systems such as multicomponent glasses.

The twofold goal of this work can be reached by combining two different levels of analysis. First, large-scale models, obtained using classical MD, are used in conjunction with experimental data to show the superiority of an SM approach to reproduce the medium-range structure of bioactive glasses. Then, smaller models are created with the specific purpose to analyze the dynamics of the melt in greater detail. By comparing the small classical models to the corresponding \textit{ab initio} reference, one can investigate local effects (short-range structure and exchange dynamics in the Si and P coordination shell), which are at least partly responsible of the different performances of SM and RI potentials on a larger scale. While a representative \(Q^n\) distribution can only be achieved using large classical models (provided that the interatomic potential is accurate), the small models are employed here to show that the inclusion of polarization effects is necessary to reach an accurate dynamic balance between the transformations occurring in the melt. Only when this favorable balance (obtained with SM potentials) is coupled with a sufficiently large system size and a lower quenching rate will the result be an accurate \(Q^n\) distribution for Si and P, which in turn is a prerequisite for large-scale simulations of the bioactivity.

## II. COMPUTATIONAL METHODS

The composition of the system was 46.2SiO\(_2\) 24.4Na\(_2\)O 26.9CaO 2.6P\(_2\)O\(_5\) mol %, roughly corresponding to the standard 45S5 Bioglass®. A large sample, described in detail below, was modeled using only the empirical RI and SM potentials, whereas a smaller sample of the same composition, also described below, was also simulated using the \textit{ab initio} CP approach, in addition to the empirical potentials. The experimental density of 45S5 glass was used for both small and large samples.

### A. Large sample

A large glass sample, including 10 017 atoms in a 51.14 Å side cubic supercell, was obtained with both RI and SM empirical potentials and used to investigate the medium-range structure of the glass and highlight the different performances of the classical potentials in relation to the available experimental data. The melt-and-quench procedure was similar to the one employed in our recent classical MD studies of different bioactive glasses. A random initial configuration (the same for the RI and SM samples) was heated to 3200 K for 100 ps and then cooled to 300 K at a nominal cooling rate of 10 K/ps, before a final room-temperature production run of 200 ps, from which the \(Q^n\) distributions of Si and P were calculated.

### B. Small sample

A smaller system containing 116 atoms in total, in a cubic periodic supercell of 11.63 Å side, was modeled using MD with the empirical SM and RI potentials, and compared to recent \textit{ab initio} data obtained with the CP method. Because the purpose of these smaller samples was to closely compare the local environments and short-range structure in the melt and the glass to the reference represented by the \textit{ab initio} data, it was important to remove any possible bias.
related to the computational setup. Therefore, exactly the same melt/quench procedure and control parameters used in the CPMD simulations were used to generate the small RI and SM samples. In this way any deviation of the small SM and RI samples from the reference CP reveals an intrinsic lack of accuracy of the specific treatment of interatomic forces, whereas the effect of the small size and fast quench rate, being the same in all the samples, will be cancelled out.

As done for the large sample, the initial configuration was created by randomly placing the appropriate number of atoms in the simulation box using shortest distance cutoffs to avoid significant overlaps. In each case, following the protocol used to obtain the CPMD reference sample, the same initial random configuration was heated up and thermalized to around 2300 K, and a microcanonical trajectory of ~14 ps was then carried out, where the temperature oscillated around 2300 K. The melt was then rapidly cooled down to room temperature through nine subsequent NVT runs of 10 ps each, with the target temperature decreased in 200 K steps. This corresponds to a nominal cooling rate around 20 K ps\(^{-1}\). Even though slower cooling rates can be easily afforded in glass simulations with empirical potentials, as explained before, this choice is dictated by the need to closely match the procedure previously used to obtain the CPMD reference.\(^3\) After the cooling phase, the system was further equilibrated at 300 K for 10 ps, before a final microcanonical production run of 12 ps. An additional MD trajectory at \(T=3000\) K was also started from the 2300 K liquid, and continued for 14 ps, the last 10 ps of which were used in the analysis, after checking the thermal equilibration of sample using the ionic mean square displacement, as discussed in Ref. \(^3\).

C. Car–Parrinello simulations

The details of the CPMD simulations can be found in Ref. \(^3\). In summary, the CP code of the QUANTUM-ESPRESSO package\(^3\) was employed, with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional\(^3\) to treat the electronic structure within density functional theory and ultrasoft pseudopotentials,\(^3\) explicitly including semicore shells for Na and Ca to represent core-valence electron interactions. The MD time step \(\delta t\) and fictitious electronic mass \(\mu\) were 7 and 700 a.u., respectively.

D. SM potential

Classical MD simulations with the SM were carried out within the adiabatic SM scheme implemented in the DL_POLY code.\(^3\) The SM interatomic potential used here, based on a potential originally developed for quartz,\(^3\) was recently adapted by us to model silicate glasses incorporating Na, Ca, and PO\(_4\) ions.\(^3\) As in standard charge-on-spring models,\(^3\) the polarizable oxide ions are represented by core-shell units of opposite charge, connected by harmonic springs. Formal, full ionic charges and short-range Buckingham potentials are used to describe the interaction of the oxygen shells with each other and with Si, Na, Ca, and P cations, and three-body screened harmonic potentials are used to control the intratetrahedral O–Si–O and O–P–O angles. In the adiabatic SM,\(^3\) the shells are given a small fraction of the core mass (0.2 a.u. for oxide ions in this work). Provided that the MD time step is chosen small enough to follow the high vibrational frequency of the core-shell units, the integration of conventional equations of motion should allow the shells to follow the ionic motion adiabatically, i.e., the total force acting on shells will constantly remain close to zero in the MD trajectory. In order to enforce this condition over relatively long time scales, it is necessary to add a damping term to the core-shell harmonic forces.\(^3\) The SM potential parameters are listed in Refs. 6 and 7.

E. RI potential

As a standard RI potential, we employed a revised version of the Teter forcefield,\(^3\) with partial ionic charges and short-range Buckingham terms for the pair interactions between oxygen and Si, P, Na, Ca, and O ions. Previous simulations\(^3\) showed that the quality of its reproduction of the structure of pure silica and sodium silicate glasses is close or slightly improved with respect to the common van Best-Kramer-van Santen (BKS) potential.\(^4\)

III. RESULTS AND DISCUSSION

A. \(Q^0\) structure

The distributions of \(Q^0\) silicate and phosphate species in the large glass samples obtained using classical MD are shown in Fig. 1. For Si, both potentials correctly lead to a predominantly \(Q^0\) structure, in agreement with experimental data,\(^3\) together with significant amounts of both \(Q^1\) and \(Q^3\) species. Even though a binary model with only \(Q^0\) and \(Q^3\) species is sometimes assumed,\(^3\) a three-component structure with \(Q^0\), \(Q^1\), and \(Q^2\) silicates turned out to provide a better fit of very recent NMR data on the 45S5 Bioglass®.\(^3\) and the
presence of more than two $Q^n(Si)$ species in this glass was also inferred from Raman spectra. Previous NMR experiments also highlighted the coexistence of several different $Q^n$ species in depolymerized alkali silicate glasses. As the presence of other species besides $Q^1$, $Q^2$, and $Q^3$ is less likely, the narrower $Q^n(Si)$ distribution predicted by the SM model, with a 10% higher $Q^2$ silicate content, and correspondingly lower amounts of $Q^0, Q^1,$ and $Q^3$, represents a closer match to the experimental results compared to the RI potential, which predicts a broader $Q^n(Si)$ distribution, similar to the one obtained using a different RI, partial-charge model. A clear improvement arising from the SM potential is also observed in the $Q^n$ distribution of phosphate species. The SM glass is dominated by isolated orthophosphate ($Q^0$) species, with a $Q^0$ abundance of 82%, and the rest of the phosphate species represented by $Q^1$ pyrophosphates, where one of the four $P-O$ bonds forms a $P-O-Si$ bridge with an adjacent silicate. On the other hand, the $Q^n(P)$ distribution of the RI glass is again much broader, with similar amounts (47% and 42%, respectively) of orthophosphates and pyrophosphates, and a significant fraction of chain metaphosphates ($Q^2$), which are not present in the SM glass. Even though the determination of the phosphate speciation in these compositions using one-dimensional magic angle spinning NMR techniques is not straightforward, recent data do suggest that a small percentage of nonorthophosphate species coexist with the majority of isolated $Q^0$ in the 455 Bioglass®. Rather than $P-O-P$, it is more likely that these species contain $P-O-Si$ bonds, on statistical grounds. As a matter of fact, the preference of for $P-O-Si$ rather than $P-O-P$ linkages was recently revealed in mesoporous bioactive glasses, using cross-polarization NMR techniques. Therefore, even if the match with the experiments can still be improved (the 17% fraction of nonorthophosphate species is presumably still too high), the SM potential provides a more accurate model of the phosphate speciation in the 455 Bioglass® compared to RI potentials. Together with the results mentioned above for the silicate $Q^n$ structure, there are clear evidences that the inclusion of polarization in the SM potential leads to consistent improvements in the medium-range structure of the glasses. The residual discrepancies are most likely related to the intrinsic limitations of the computational procedure used to make the glass: namely, the limited size of the periodic supercell, which imposes artificial constraints due to the periodic boundaries, and the much faster cooling rate used in the simulations than in the experimental melt-and-quench procedure. For the purpose of the present paper, in the following, we will focus on understanding the microscopic origin of the improvements to the final glass structure brought about by the SM potential. We will investigate how the inclusion of polarization in the model affects the structural evolution from the melt to the glass. As explained before, the reference system is represented in this case by a small periodic sample where the interatomic forces are treated with ab initio accuracy. Even though the absolute $Q^n$ amounts of these systems cannot be representative of a macroscopic sample, important insight is provided by the short-range structure and the dynamics of the exchanges in the Si/P coordination environment during the high-temperature trajectory.

**B. Local (short-range) structure**

First, we examine the short-range atomic arrangements of the amorphous system and its melt precursor in order to highlight even small differences which can play a role in the process of glass formation from the melt. The radial distribution functions (rdfs) of the melt modeled using SM, RI, and CP approaches are shown in Fig. 2. In the melt, the rdfs obtained using the two interatomic potentials are rather similar to each other. The most significant difference with respect to the CP rdfs is the $Si-Si$ distribution, which in the ab initio sample has a short-distance tail extending to 2.2 Å, whereas no such short $Si-Si$ contacts are formed in the MD runs using the classical potentials. Moreover, while the peak positions of the classical and ab initio rdfs are rather close, the latter tend to be broader than the corresponding SM and RI ones, denoting a larger degree of structural disorder in the ab initio melt. In fact, Table I shows that a larger fraction of $Si_{4c}$ and $Si_{5c}$ ions are found on average in the CPMD melt, compared to both melt samples obtained with the classical potentials. We have previously observed that some of these

**TABLE I.** Average Si coordination (%) in 3000 K melt. Standard errors are reported between parentheses.

<table>
<thead>
<tr>
<th></th>
<th>$Si_{2c}$</th>
<th>$Si_{3c}$</th>
<th>$Si_{4c}$</th>
<th>$Si_{5c}$</th>
<th>$Si_{6c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM</td>
<td>0</td>
<td>0.7 (0.07)</td>
<td>97.2 (0.1)</td>
<td>2.3 (0.06)</td>
<td>0</td>
</tr>
<tr>
<td>RI</td>
<td>0</td>
<td>1.7 (0.05)</td>
<td>96.5 (0.1)</td>
<td>1.8 (0.05)</td>
<td>0</td>
</tr>
<tr>
<td>CP</td>
<td>0.1 (0.01)</td>
<td>5.5 (0.08)</td>
<td>88.8 (0.1)</td>
<td>5.5 (0.08)</td>
<td>0.1 (0.01)</td>
</tr>
</tbody>
</table>

*Fig. 2. (Color online) rdfs of the small melt samples (3000 K) modeled using the classical SM and RI interatomic potentials and the CPMD approach.*
defects are found in or are associated with small rings containing two or three silicon ions.\cite{31} Even though the small size of the samples does not allow us to draw more quantitative conclusions, the CP melt at 3000 K is certainly characterized by a more distorted local structure. This is further highlighted in the bond angle distributions (BADs) in Fig. 3. The O–Si–O angle distribution of the CP melt is broader and with a tail extending to lower angles. The intertetrahedral Si–O–Si angle in the CP distribution is also significantly broader, due to a shoulder around 90\degree, which corresponds to the short-distance tail in the Si–Si rdf mentioned above\cite{31} and is absent from the SM and RI BADs. These additional features in the CP BADs are mostly associated with the higher fraction of structural defects.\cite{31} It is important to remark that in agreement with previous results for soda-lime silicate glasses,\cite{22} the SM potential seems to provide a better description of the intertetrahedral geometry of the silicate network in the melt, with its main intertetrahedral peak shifted significantly closer to the CP reference than the RI potential. Except for the latter observation, both classical potentials show some inadequacy in the description of the considerably distorted short-range structure of the melt, highlighted in the CP simulations. This reflects the fact that the RI and SM potentials are fitted to the structural properties of crystalline oxides.\cite{6} Even though they are transferable to amorphous phases, the classical potentials are not completely able to reproduce local environments which are not commonly found in the low-temperature solid because by construction they are biased against large distortions in bond distances and angles. On the other hand, the rdfs of the glass (Fig. 4) confirm the superiority of a potential including polarization to model glass structural features, not only in the medium range, as shown in the previous section, but also in the short range. The CP rdfs for the glass can be used again as a direct reference, unbiased by system-size effects, which were carefully screened out thanks to the procedure discussed before. The SM provides a closer match to the \textit{ab initio} data for essentially all the atomic pairs whose rdfs are shown in Fig. 4. This trend is summarized in the total distribution functions $T(r)$ (Ref. 22) shown in Fig. 5, which denote a rather poor performance of the RI potential in the 2–4 Å range, where the nonbonded nearest neighbor interactions are represented. The $R_\text{v}$ factors,\cite{48} calculated with respect to the CP $T(r)$, are 9.6\% and 17.2\% for the SM and RI potentials, respectively, confirming the better performance of the SM potential also in reproducing the short-range structure of the glass. Some of the characteristic distances and angles are collected in Table II. The SM potential provides a more accurate representation of the different strength of $T$-NBO and $T$-BO bonds, where $T$ is a network-former atom, i.e., Si or P. In particular, the \textit{ab initio} and SM models yield $T$-BO bonds 0.07–0.08 Å longer than $T$-NBO, whereas the difference is only 0.04 Å for the RI potential. Both classical potentials predict an average Si–O distance slightly shorter, but close to the experimental estimate of 1.61 ± 0.02 Å (Refs. 4 and 49) (RI and SM potential yield 1.59 and 1.60 Å, respectively), whereas the \textit{ab initio} Si–O mean distance is 1.625 Å; therefore both classical potentials appear to provide an accurate average description of the Si–O bond. The inclusion of polarization does not improve the average Si–O distance, which is already accurate without polarization, but seems to be im-

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**FIG. 3.** BADs of intratetrahedral ($\text{O}$SiO) and intertetrahedral ($\text{Si}$–O–Si) angles of the 3000 K melt samples obtained with the classical SM and RI interatomic potentials and with CPMD.

**FIG. 4.** (Color online) rdfs of the small glass samples obtained with the classical SM and RI interatomic potentials and with CPMD.

**FIG. 5.** (Color online) (Top panel) Total distribution function $T(r)$ of the small glass samples obtained with the classical SM and RI interatomic potentials and with CPMD. (Bottom panel) Corresponding error $T'(r) - T^\text{CP}(r)$, where $I=$SM or RI.
TABLE II. Glass short-range structure. Selected average distances (Å) and angles (deg) involving BO and NBO atoms. Values within parentheses are coordination numbers, calculated by integrating the corresponding rdf up to the first minimum cutoff (3.1 and 3.2 Å for Na–O and Ca–O, respectively). Estimated uncertainties for all reported values are ±1% (±0.01 Å and ±0.5° for distances and angles, respectively).

<table>
<thead>
<tr>
<th></th>
<th>SM</th>
<th>RI</th>
<th>CP</th>
</tr>
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<tbody>
<tr>
<td>$r_{\text{Si-NBO}}$</td>
<td>1.58</td>
<td>1.58</td>
<td>1.60</td>
</tr>
<tr>
<td>$r_{\text{BO}}$</td>
<td>1.66</td>
<td>1.62</td>
<td>1.67</td>
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<tr>
<td>$r_{\text{P}}$</td>
<td>1.54</td>
<td>1.48</td>
<td>1.55</td>
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<tr>
<td>$r_{\text{P-BO}}$</td>
<td>1.61</td>
<td>1.52</td>
<td>1.63</td>
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<tr>
<td>$r_{\text{NBO-NBO}}$</td>
<td>2.63</td>
<td>2.42</td>
<td>2.67</td>
</tr>
<tr>
<td>$r_{\text{NBO-BO}}$</td>
<td>2.67</td>
<td>2.61</td>
<td>2.70</td>
</tr>
<tr>
<td>$r_{\text{BO-BO}}$</td>
<td>2.63</td>
<td>2.60</td>
<td>2.63</td>
</tr>
<tr>
<td>$\theta_{\text{BO-Si-NBO}}$</td>
<td>113</td>
<td>110</td>
<td>112</td>
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<td>$\theta_{\text{BO-Si-NBO}}$</td>
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<td>108</td>
<td>110</td>
</tr>
<tr>
<td>$\theta_{\text{BO-Si-BO}}$</td>
<td>106</td>
<td>107</td>
<td>105</td>
</tr>
<tr>
<td>$r_{\text{Na-NBO}}$</td>
<td>2.33 (4.0)</td>
<td>2.38 (4.6)</td>
<td>2.28 (4.0)</td>
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<tr>
<td>$r_{\text{Na-BO}}$</td>
<td>2.45 (1.6)</td>
<td>2.52 (1.0)</td>
<td>2.46 (1.4)</td>
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<td>$r_{\text{Ca-NBO}}$</td>
<td>2.27 (5.5)</td>
<td>2.38 (5.4)</td>
<td>2.30 (5.8)</td>
</tr>
<tr>
<td>$r_{\text{Ca-BO}}$</td>
<td>2.59 (0.4)</td>
<td>2.73 (0.8)</td>
<td>2.42 (0.4)</td>
</tr>
<tr>
<td>$\theta_{\text{O–Na–O}}$</td>
<td>59–91</td>
<td>57–87</td>
<td>60–91</td>
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<tr>
<td>$\theta_{\text{O–Ca–O}}$</td>
<td>62–85</td>
<td>58–85</td>
<td>65–81</td>
</tr>
</tbody>
</table>

important in determining the correct balance between Si-BO and Si-NBO distances within the SiO$_4$ tetrahedra. The better intratetrahedral geometry of the SM is also evident from the (N)BO-(N)BO distances and (N)BO-Si-(N)BO angles in Table II, which are significantly closer to the corresponding CP values than those yielded by the RI potential. In particular, the SM produces a more marked difference between O–Si–O angles formed by two NBOs and by two BOs, again in close agreement with the CP data. When we examine the coordination environment of modifier Na and Ca cations in Table II, the description provided by both classical potential appears fairly accurate, and slightly closer to the CP data in the case of the SM potential. For the purpose of the present work, the present comparison shows that a SM provides a realistic description of the distorted tetrahedral shell of Si and P, with an accurate representation of the different bonding patterns involving BOs and NBOs. Despite the slightly less accurate performance in this context, RI potentials can be considered sufficiently adequate in the case where the interest is primarily in modeling the short-range structure of these materials; however, the SM should be the method of choice when an accurate description of the medium-range structure and network connectivity is sought.

C. Temperature-dependence of the $Q^n$ structure

We have seen in the previous section that the better performance of the SM potential in reproducing both the short- and medium-range structure of the melt-derived glass does not reflect a (significantly) more accurate description of the melt precursor compared to the RI potential. As the accuracy of the structural model of the melt precursor itself does not appear crucial for the quality of the final glass structure, we examined the time evolution of the system during the cooling in order to understand where the inclusion of polarization positively impacts the model of the glass formation. The changes in the Si coordination, as well as in the $Q^n$ distributions, as the melt is gradually cooled to room temperature are highlighted in Fig. 6. At this stage, it is worth noting again that a more significant test of the medium-range structure is provided by the large glass samples discussed before, and the absolute $Q^n$ abundancies of the small samples should not be considered representative of the specific performances of the SM and RI potentials from this perspective. However, the comparison of relative trends in the modeled melts does provide relevant insight. In particular, the small models incorporate an accurate representation of local effects that can influence the extended network connectivity in larger samples, such as the exchange dynamics in the coordination shell of Si and P. The advantage of performing three additional sets of calculations with a smaller sample is that we can now directly compare the dynamical trends emerging from the melt-quench trajectory as the system is cooled, with the accurate reference represented by the CP system. The left panels in Fig. 6 show that, starting from the melt at 3000 K, during the cooling the CP and SM systems evolve in a similar and consistent way, with a decrease in $Q^4$ and corresponding increase in $Q^2$ and $Q^3$ as the melt is cooled down. On the other hand, in the RI system, the opposite $Q^2 \rightarrow Q^4$ transformation is taking place instead, while at the same time, the initial small amount of $Q^4$ silicates is not further transformed during the cooling phase and is still found in the glass, whereas all $Q^4$ are converted into lower-$n$ $Q$ species in the CP and SM runs. The main message that can be gathered from Fig. 6 is that the dynamical behavior of the high-
temperature RI model is rather different from the reference CP, whereas the SM model appears to follow more closely the \textit{ab initio} data. This seems to indicate that the less accurate \(Q^n\) distribution of the large RI samples might be a consequence of some inadequacy of the RI potential to describe the melt-quench process.

Figure 7 shows several snapshots extracted from the CP-MD trajectory at 3000 K, highlighting the changes in the \(Q^n\) connectivity of a selected Si ion. The initial \(Q^3\) coordination of the tagged Si (panel a) changes to \(Q^2\) in (b) by forming a Si–O–Si bridge with an adjacent Si, which keeps its tetrahedral coordination by losing a bonded BO to another adjacent Si. When the latter bond is reformed as in (c), the result is a 4-M ring containing a fivefold-coordinated Si adjacent to the tagged \(Q^2\) Si. Internal rearrangement of this complex, with the formation of a Si–O–Si bond between the \(Q^2\) Si and the opposite Si in the ring, reduces the size of the ring to a 3-M ring still containing an Si5c (panel d). The latter species then recovers fourfold coordination when one of its oxygens is captured by a neighboring Si (this O can still be spotted in the bottom right of panel e), and a fully saturated 3-M ring is formed (panel e). This ring is then further transformed due to the interaction of the tagged \(Q^2\) Si with another adjacent Si, which becomes fivefold coordinated while the tagged Si becomes \(Q^3\) (f). Again, the tetrahedral coordination is restored by removal of an extra oxygen (top right of panel g), and the final result is a \(Q^3\) Si still incorporated in the 3-M ring (g). Finally, the 3-M ring is opened due to the action of an orthophosphate group, which donates one of its NBOs to form a new P–O–Si link (h), which then replaces the Si–O–Si bridge in the ring, thus converting the tagged Si back to \(Q^2\) (i). These complex rearrangements take place in less than \(\sim 10\) ps and show how the transient formation of coordinative defects (especially Si5c) and small rings bring about frequent changes in the \(Q^n\) speciation. The active participation of structural defects to the interconversion between \(Q^n\) species in silicate melts had been previously proposed.\(^{51}\)

Due to their established role in the \(Q^n\) transformation, it is important to see how the fraction of undercoordinated and overcoordinated Si also changes during the cooling phase, especially because, as noted before, the overall fraction of these defects found in the 3000 K melts modeled with both classical potentials was reduced with respect to the CP reference. The data shown in the right panels of Fig. 6, while confirming that a higher fraction of defects is always present in the CP melt, also show that most defects have been healed in the RI sample already at 1800 K, whereas a non-negligible percentage of fivefold-coordinated Si defects is still present in the SM sample at lower temperatures, until no residual defects are left below 1200 K. This interesting trend was confirmed in the larger system. Figure 8 shows that the decay of the initial total fraction of miscoordinated Si and P is faster in the RI than in the SM sample, in which a higher fraction of defects is always present during the cooling. These observations seem to denote a correlation between a more accurate description of the medium-range structure of the glass and the persistence of miscoordinated atoms during the cooling, which can assist the interconversion process between the \(Q^n\) species.

D. Dynamics of \(Q^n\) interchanges

The interchange between the various \(Q^n\) species can be further analyzed by focusing on the dynamics of \(Q^n \leftrightarrow Q^{n+1}\) transformations in the melt. The characteristic time for the \(Q^n \leftrightarrow Q^{n+1}\) transformations, with \(n=1, \ldots, 4\) was averaged over all such processes completed in the MD trajectories at \(T=3000\) K. The statistics are summarized in Table III. An important point highlighted in the table is the more facile nature of \(Q^n \leftrightarrow Q^{n+1}\) processes in the CP melt, where all transformations occur faster, and therefore a larger number of interconversions is completed in the same simulation time, compared to the SM and especially to the RI run. The slower dynamics of \(Q^n\) interchanges with the RI potential might denote an important role of polarization effects in accounting for these transformations in a more realistic way, even though their rate in the SM system is still lower than in the

![FIG. 7. (Color online) A series of snapshots extracted from the CP-MD trajectory at 3000 K, showing the mechanism of the changes to the \(Q^n\) speciation of a selected Si. The atoms involved in the transformations are highlighted as ball and stick. Color codes areas follows: Si (turquoise), O (red), Na (gray), Ca (green), and P (yellow).](image-url)
reference CP system, as to indicate that additional effects would need to be incorporated in the classical potentials for further improvement.

For each transformation, the $K_{n,n+1}$ ratio between the measured $Q^{n+1} \rightarrow Q^n$ and $Q^n \rightarrow Q^{n+1}$ mean times is also reported. These ratios are used to assess the relative stability of two $Q^n$ species in the melt based on the time it takes on average to be converted into one another. The data in the Table III show that the formation of $Q^2$ from $Q^1$, as well as from $Q^3$, is strongly favored in the CP and SM cases, whereas with the RI potential the $Q^2 \rightarrow Q^3$ transformation is on average faster than the inverse process. The same analysis was then repeated in the 2000–1400 K range, in which Fig. 6 denoted a significantly different behavior of the RI potential with respect to the SM one and the CP simulations. In this range, the $K_{1,2}$ and $K_{2,3}$ values are 3.2 and 0.54 for CP, 7.5 and 0.66 for SM, and 0.98 and 3.1 for RI, respectively. Despite the different absolute values, the SM shows the correct trend, favoring the formation of $Q^2$ from both $Q^1$ and $Q^3$, whereas in the same temperature range, which is crucial for the glass formation, the RI potential is biased toward a depletion of the $Q^2$ abundancies in the system, in favor of $Q^1$ and $Q^3$. Even though the equilibrium $Q^n$ speciation does not necessarily reflect the $K_{n,n+1}$ ratios, there is some evidence that the dynamical and energetic interaction between the $Q^n$ species in the melt is better described when polarization is included.

### IV. SUMMARY AND FINAL REMARKS

The present simulations show that the approximate inclusion of polarization in the interatomic potential results in significant improvements in the intertetrahedral structure of melt-derived multicomponent glasses, and is therefore essential to model processes where the glass network connectivity plays a crucial role, such as the dissolution and reactivity in physiological environments and technological applications. The physical reasons for these improvements are not related to a better description of the melt precursor, for which the classical potentials, with and without including polarization, do not fully reproduce the highly distorted short-range structure highlighted by CP simulations. Despite this discrepancy, which reflects the intrinsic bias of the classical interatomic potentials toward “regular” local arrangements, the structure of the glass obtained upon cooling the melt with the SM potential is significantly improved, not only in the medium-range as mentioned before, but also in the short-range. In particular, the inclusion of polarization improves the intratetrahedral geometry as a consequence of a more realistic treatment of $T$-BO and $T$-NBO bonds.

Because the structure of the melt is not improved with the SM, whereas the final glass structure is, including the polarization of oxide ions seems to be essential to steer the melt $\rightarrow$ glass transformation upon cooling in a more reliable way. This hypothesis was confirmed by examining smaller samples of this system, whose atomistic properties could be directly compared to a reference $ab\ initio$ model of the same size. The analysis of interchanges between the $Q^n$ species as a function of the temperature denotes a higher stability of $Q^2$ species during the cooling with the SM potential, in agreement with the CP data, whereas the dynamical evolution of the melt with RI potential reveals a lower stability of $Q^2$ species already in this precursor phase. In particular, despite the faster rates measured in the CP dynamics, the inclusion of polarization in the SM potential determines sufficiently accurate rates of interconversion between the different $Q^n$ species.

In order to model the glass medium-range properties such as the $Q^n$ distribution, periodic samples of large size must be obtained, which rule out $ab\ initio$ MD and impose the use of classical MD. The $ab\ initio$ MD sample was used in this work mainly to provide an unbiased reference for the local interactions occurring at high temperature. This comparison highlighted the more realistic behavior of the SM melt. It is only when this accurate local balance is combined with a large system size that an accurate $Q^n$ distribution for both Si and P can be obtained. There are some indications that the better performances of the SM potential reflect its ability to allow the persistence also at lower temperatures of a small amount of miscoordinated Si defects, which are involved in the interconversion process of $Q^n$. In addition, larger-scale CPMD simulations would be needed to further test and confirm this hypothesis.

In conclusion, in this work we have shown that the inclusion of polarization effects at the level of a SM potential is essential to model multicomponent silicate glasses, whereas more sophisticated force fields might be needed to accurately model the corresponding melts, especially if a very accurate description of structural and coordinative distortions at high temperature is sought. Possible reasons behind the improved glass structure provided by the SM were discussed, such as the persistence of fivefold-coordinated Si at lower temperatures, which in turn might lead to the quali-
tatively accurate balance between the dynamical processes of interconversion between the $Q^n$ species during the cooling phase.

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30. The $Q^n$ notation denotes a TO$_4$ tetrahedron (T=Si or P) with $n$ BOs. The theoretical $Q^n$ distribution is obtained from the MD trajectories by first determining the local coordination shell of Si and P atoms at each time step (using a distance cutoff of 2.25 Å to identify T-O bonded pairs), from which the determination of the $Q^n$ distribution is straightforward.
42. For comparison, critical cooling rates between 20 and 50 K/min have been measured for alkali silicate glasses (Ref. 47).
46. The bimodal $Q^n$ distribution of the small RI sample is in fact anomalous, and large samples, such as those discussed in Sec. III A, are needed to produce a $Q^n$ distribution representative of the actual performances of the potentials in this range. At the same time, the small samples can still provide an adequate representation of the local dynamics of the individual $Q^n$ species.
48. In silicate melts, the equilibrium $Q^n$ amounts reflect disproportionation reactions involving more than two species (Ref. 53), and therefore there is no straightforward thermodynamic relationship between the $Q^n$ amounts and the $K_{eq,n}$ ratios reported in Table III.