Efficient generation of realistic model systems of amorphous silica

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We used classical molecular dynamics and the van Beest Kramer van Santen (BKS) potential to generate small model systems of amorphous silica. We further optimized the classically equilibrated configurations using plane wave based density functional theory and a generalized gradient (GGA) approximation. Within ab initio treatment we showed that both geometry optimization and Car-Parrinello annealing lead to the same final configurations but the CPU time required for the geometry optimization to reach convergence is one fifth of the time needed by a Car-Parrinello annealing. In addition during the optimization or the annealing no substantial change occurs on the topology acquired by the vitreous silica at the end of the classical quenching protocol. Structural and electronic properties have been calculated and compared to experiments.

I. INTRODUCTION

Disordered forms of silicon dioxide (SiO$_2$) glasses play a key role in electronic device applications like semiconductor devices and optical fibers. Amorphous silica has a structure consisting of a continuous random network of corner-sharing SiO$_4$ tetrahedra linked to a continuous three dimensional network. Numerical simulations in the framework of classical molecular dynamics (MD) has allowed in the past to clarify several issues connected with the structural properties of this material at the microscopic level. Basis of this approach are interaction potentials fitted to ab initio and experimental parameters. Density Functional Theory (DFT) provides instead a description of both the electronic and ionic degrees of freedom and represents a powerful tool to study disordered systems. Indeed, this approach allows to improve the description of the structure and gives access to the electronic properties of amorphous SiO$_2$ (α-SiO$_2$). Car-Parrinello molecular dynamics (CPMD) simulation allows to study dynamical properties of the system within DFT. During the nuclear dynamics, the wavefunction remains sufficiently close to the Born-Oppenheimer surface allowing a faithful description of the electronic structure in most standard situations. However, the treatment of the dynamics of disordered systems in an ab-initio way is extremely costly from a computational point of view. This imposes restrictions to the size of the systems that can be studied and on the maximum length of the trajectory that can be calculated in a molecular dynamics simulation. The length of the trajectory that can be obtained within the Car-Parrinello method (CPMD) is of the order of picoseconds. In order to overcome these limitations different simulation strategies have been adopted in the past that combine the advantages of classical dynamics and the accuracy of an ab initio description. Among these, the methodology exemplified in a paper by Ginovsken et al. has been validated in a very accurate way. Through the comparison of several combinations of classical and density functional schemes, the authors show that small systems of α-SiO$_2$ (under 100 atoms) exhibit local structural characteristics that are similar to those of larger systems. Benoit et al use classical molecular dynamics for annealing small samples at very high temperatures (above $T = 3000K$), quench the liquid up to a glassy transition, and then refine their analysis with a CPMD dynamics run followed by CPMD quenching to find a minimum energy structure. However, the work of Benoit et al. still leaves space for improvement. In this paper we propose an enhanced protocol based on the same philosophy, but with a few important differences. First of all we use an improved classical potential, suitable for high temperature phases. Subsequently, our CPMD quenching protocol, particularly suited for the amorphous samples of small size shows to be more efficient than the one used in the past. Finally, we provide an interesting insight into the ring analysis by doing energetical considerations that should help to assess the validity of amorphous samples generated with this method. This work shows how to efficiently generate small systems that still well represent the properties of infinite sized samples. The procedure described in this paper reduces the amount of CPU time required for the generation of α-SiO$_2$ by about a factor of five with respect to without compromising the final results. The properties of these system models are in good agreement with fully ab initio model systems and with available experimental data.

II. COMPUTATIONAL SETUP

Our starting model was a slightly deformed cell of 72 atoms in the solid α-quartz phase. We adopted periodic boundary conditions (PBC) in all directions in order to mimic the bulk behavior. The PBC scheme allows to reduce finite size effects as well as surface effects and to get realistic properties with a small simulation cell. The model of the amorphous phase α-SiO$_2$ was obtained by first melting the quartz cells and then quenching from the melt using classical molecular dynamics with step cooling.
The classical MD calculations were performed using the MOLDY package. The long range electrostatic forces were treated using the Ewald technique. We classically modeled the interaction between atoms using the empirical potential introduced by van Beest et al. (BKS), which has been shown to properly describe the structural and dynamical properties of amorphous silica. This potential is a two body interaction consisting of a Coulomb term and a short range term cast in the usual Buckingham form. Only two short range interactions are taken into account: the Si-O interaction which describes the silica bond and the O-O non bonded interaction which causes the tetrahedral arrangement of oxygen atoms around the silicon atom. At short distances the BKS potential diverges attractively limiting its use in molecular dynamics runs at high temperature (in our case above 3700 K). In order to avoid this divergence at short distances we add a repulsive term. This modification is necessary to describe the high temperature liquid where ions of opposite charges would otherwise approach each other very closely and be trapped in the well of the Coulomb potential. The functional form of the potential adopted in the classical simulations is therefore:

\[ V_{ij} = \frac{e^2}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} + A_{ij} e^{-\bar{r}_{ij}} - \frac{C_{ij}}{r_{ij}^6} + \frac{D_{ij}}{r_{ij}^{12}} - \frac{E_{ij}}{r_{ij}^8} \]

where the first three terms represent the standard BKS potential and the last two terms the correction introduced to avoid the divergence at short distances. The force field parameters for the BKS potential are reported in Table I. In Table II we report the coefficients of the correction terms applied and in Fig. 1 we plot the original potential and the last two terms the correction introduced. These additional terms do not change the physics of crystalline and amorphous phases.

DFT calculations were performed using the CPMD software. The electronic structure has been treated using plane waves (PW) basis sets and pseudopotentials. The use of PW has several advantages. PW call for the use of PBC and the atomic forces can be computed via the Hellman-Feynman theorem without evaluating the Pulay contributions. In addition the convergence of total energy and force calculations can be controlled by a single parameter (kinetic energy cutoff) and improved to arbitrary accuracy. We made use of the Generalized Gradient approximation (GGA) to describe the exchange-correlation energy. Core-valence interactions have been described through norm-conserving pseudopotentials for both oxygen and silicon atoms. We used a plane wave basis set defined by an energy cutoff of 70 Ry for plane waves and 280 Ry for the electronic density which has...
been shown to be large enough to insure the convergence of
the energy, in some preliminary tests on α-quartz and
β-cristobalite. The Brillouin zone has been sampled at
the Γ point only\textsuperscript{16}. All the Density Functional calculations
have been performed with PBC in all three spa-
tial directions and keeping the volume of the supercell
costant.

III. MODEL SYSTEMS AND QUENCHING
PROTOCOL PROCEDURE

An orthorombic simulation cell of crystalline α-quartz
containing 72 atoms of Oxygen and Silicon (24 SiO\textsubscript{2} units)
have been rescaled in the \( x, y \) and \( z \) direction making it
cubic and matching the amorphous SiO\textsubscript{2} experimental
density of 2.20 gr/cm\textsuperscript{3}. The so obtained configuration
has been used as the starting supercell for the simu-
lations. The size of this periodically repeated cubic super-
cell was 10.29 Å.

In the classical MD simulations the equations of motion
for the ions were integrated using a modified version of
the Beeman algorithm as implemented in MOLDY\textsuperscript{2}\textsuperscript{23} with
a timestep of 1.6 fs. In total seven amorphous silica
model systems were generated. During the simulations
all the atoms within the supercell have been allowed to
move while the volume of the supercell has been kept
fixed. The starting configurations have been heated up
rapidly to \( T = 8500 \) K leading to the formation of liq-
uid silica. We subsequently performed a 25 ps costant
temperature run at \( T = 8500 \) K in order to equilibrate
these high temperature liquids. We then quenched the
model systems to \( T = 300 \) K using constant tempera-
ture MD runs performed at different temperatures, with
a final averaged quenching rate of \( 1.6 \times 10^{12} \) K/s. The
quenching protocol is reported in Fig. 2. It is impor-
tant to notice that the quenching rate should be not too
high. Very high quenching rates hinder an adequate re-
lexation, and can eventually freeze the concentrations of
small rings (see section IV) to values much higher than
those experimentally expected. During all the costant
temperature runs the velocities of the particles were peri-
dically rescaled assuming a Maxwell-Boltzmann distri-
bution at the target temperature. We noticed from the
mean square displacements of the Si and O atoms, that
the freezing temperature of these model systems can be
located around \( T = 3300 \) K, which is much larger than
the experimental data. The resulting structures were
perfectly ordered with every silicon atom fourfold and
every oxygen atom twofold coordinated. The final con-
figurations were equilibrated classically at \( T = 300 \) K
for about one nanosecond. We finally performed a 0.5
picosecond microcanonical Car-Parrinello molecular dy-
namics run on the equilibrated systems (\( T = 300 \) K)
in order to get configurations for structural analysis and
comparison with the classical model systems. The anal-
ysis of the structural properties is reported in section VI.

FIG. 2. Quenching protocol used in this work for the gen-
eration of the amorphous SiO\textsubscript{2} model systems.

IV. AB INITIO STRUCTURAL RELAXATION

The configurations obtained as described in the pre-
vious section have been further optimized by explicitly
treating the electronic degrees of freedom with DFT.
DFT combined with Molecular Dynamics offers several
methods for structure relaxation and global optimization.
In this section we describe the effects of geometry opti-
mization (G.O.) and Car-Parrinello simulated annealing
(CP annealing) of the model systems. G.O. and CP an-
nealing represent two different ways to reach the equi-
librium configuration of a given system. In a G.O. one
starts with a given structure characterized by the nuclear
coordinates. By evaluating the forces for that set of nu-
clear coordinates one gains information on how to shift
the atomic positions in order to reduce the total energy.
The procedure is repeated until the structure does not
change any further within a predefined tolerance. An
alternative approach is the CP annealing. Within this
method the electronic and nuclear degrees of freedom
are optimized simultaneously, starting the calculation at
a given temperature. Then the temperature is reduced
gradually and the structure should get trapped in that
of the global energy minimum with a higher probability
and not in a local one\textsuperscript{16}. This method has been shown to
be successful for large systems where the energy surface
is extremely frustrated.

When switching from the Classical MD treatment to the
ab-initio description, a common way to treat the system
is to first perform a sufficiently long constant tempera-
ture (NVT) run, say at \( T = 300 \) K for equilibration, and then
anneal to a \( T = 0 \) K configuration to reach the ground
state energy of the system\textsuperscript{16,17}. This procedure costs a lot
of CPU time (in\textsuperscript{16} larger systems have been studied).
We noticed that, at least for these small systems, a G.O.
and a CP annealing lead to the same final configuration,
but the CPU time required for the G.O. to reach con-
vergence is one fifth of the time needed by a CP annealing
(see Fig. 3). In addition during the optimization or the
annealing no substantial change occurs on the topology
acquired at the end of the classical quenching protocol.
The root mean square displacement (RMSD) between the
final configurations obtained within G.O. and CP anneal-
FIG. 3. Total energy of the system versus the CPU time in seconds with four processors. The upper graph shows the behaviour of the system in a geometry optimization, and the lower graph shows the behaviour in a Car-Parrinello simulated annealing.

TABLE III. CPU time in seconds with four processors needed to relax the system to its ground state as a function of the number of time steps of the initial CP run.

| Step | CP (s)  | 0  | 100 | 200 | 300 | 500 | 700 | 1000 |
|------|---------|----|-----|-----|-----|-----|-----|------|
|      | G.O. (s)| 9731 | 9340 | 10059 | 9602 | 6819 | 5779 | 0 |
| Total|         | 9731 | 11654 | 14687 | 16545 | 18391 | 21980 | 46289 |

One way to characterize SiO$_2$ networks is by studying the statistics of closed rings of bonded atoms. An $N$ ring is described as a closed Si-O-Si-O- chain with $N$ silicon atoms. Small rings ($N=2$ or $3$) are geometrically strained structures and result in an energy penalty. During the cooling protocol unrealistic geometry structures can occur. Two reasons for the appearance of such unphysical structures are the limited size of the computational box (72 atoms) and the applied PBC. In addition a too high quenching rate can prevent an appropriate relaxation of the model systems and freezes the concentration of small rings. Unrealistic model systems exhibit the presence of large voids and compressed regions within the simulation box or concentrations of small membered-rings much higher than the experimental ones. While large voids can be consistent with the structure of amorphous silica, the high density of compressed regions of the cell is not. For these reasons we generated several model systems of $a$-SiO$_2$ and selected the ones which satisfied all the criteria of a realistic structure. A primary criterion for selecting the systems was to compute the total energy and eliminate the model systems with higher energies corresponding to higher stresses. As a consequence of this criterion systems which exhibited a too high concentration of small rings, which are strained structures, have been eliminated. Among seven generated systems only one was eliminated because it showed a too high concentration of small rings confirming that the quenching protocol adopted was slow enough for an appropriate relaxation of the amorphous configurations.

The three-membered rings are quasiplanar as can be deduced from the sum over all bond angles in the rings that average to 702°, while the ideal value is 720°. The average Si-O-Si angle in these rings is 131°80' which is smaller than the average of 147° of the model systems. The average Si-O bond lengths is 1.642 Å in agreement with. Four-membered rings do not exhibit preferences for planarity; the sum over all bond angles in the rings give an
TABLE IV. In the second column $\Delta E$ is the difference of the total energy of the model systems to the one with the lowest energy. In the other columns number of n-rings in the model systems.

| models  | $\Delta E$ (eV) | 2-R | 3-R | 4-R | 5-R | 6-R | 7-R | 8-R |
|---------|----------------|-----|-----|-----|-----|-----|-----|-----|
| model-1 | 1.15           | 0   | 1   | 1   | 1   | 1   | 1   | 0   |
| model-2 | 1.65           | 0   | 3   | 1   | 2   | 0   | 1   | 1   |
| model-3 | 0.7            | 0   | 0   | 1   | 1   | 3   | 2   | 1   |
| model-4 | 0              | 0   | 0   | 1   | 1   | 2   | 1   | 0   |
| model-5 | 0.44           | 0   | 0   | 2   | 1   | 2   | 1   | 1   |
| model-6 | 1              | 0   | 2   | 1   | 3   | 2   | 1   | 0   |
| model-7 | 1.2            | 1   | 2   | 1   | 4   | 3   | 1   | 0   |

angle of 976.88° (ideal 1080°) while the average Si-O-Si angle is 137.02°, which is smaller than the reference angles inferred from NMR measurements (145°–150°) or from x-ray diffraction experiments (144°–150°)\(^{26}\). In table IV we report the differences $\Delta E$ of the total energy of the model systems to the one with the lowest energy, which we called model-4. In the other columns we give a description of the systems in terms of ring statistics. As can be seen from the table the systems with higher energies and stress are that ones with a higher concentration of small rings, showing that the presence of small rings is the main cause of stress in the system. We estimated an upper bound for $\Delta E$ of 1 eV per small rings (2,3 membered rings) which is in agreement with\(^{24}\), considering the fact that in addition to the penalty energies coming from the strained rings other sources for stress can be the fact that during all the simulations the volume of the computational box has been kept fixed.

VI. STRUCTURAL PROPERTIES

Among all the generated SiO$_2$ model systems we selected the model-4 which best satisfied our criteria for a detailed study. This choice has been performed on the basis of the ring analysis of the previous section, but further analysis has to be performed to validate this finite size sample. The most natural way to further estimate the quality of the generated amorphous model systems is to analyze their structural characteristics such as bond lengths and angle distributions, radial distribution functions, static structure factors and to compare them to available experimental data. We evaluated all these properties for the system called model-4. At $T = 300$ K we have calculated the time-averaged distributions of the intra-tetrahedral O-Si-O and inter-tetrahedral Si-O-Si angles for the classical and quantum MD simulations using the same starting configuration (Fig. 5). The intra-tetrahedral angles O-Si-O stay close to the experimental value of 109.4° for both simulations: 109.3° ± 5 for the classical and 109.5° ± 7 for the CPMD. The only difference between the classical and quantum simulation of the angle distribution is a small shift of the mean value of the intra-tetrahedral Si-O-Si angle. We estimated for this angle a mean value of 152° ± 11° for the classical averaged configurations and 146° ± 6° for the Car-Parrinello microcanonical run (NVE) (the experimental value being 140°–150°)\(^{22}\). We noticed that this change in angle takes place during the first steps of the Car-Parrinello run corresponding to an extremely short sampling time ($\approx 0.07$ ps).

We have then calculated the averaged pair correlation functions $g_{\alpha\beta}(r)$, where $\alpha, \beta = $ Si, O of the systems at $T = 300$ K for the Classical and Car-Parrinello runs (Fig. 6). Within the classical treatment we obtained an averaged distance of 1.61Å for Si-O, 3.12Å for Si-Si, and 2.66Å for O-O, in very good agreement with the experimental data\(^{22}\). For the Car-Parrinello treatment the averaged bond length Si-O is found to be 1.65Å, which is slightly (3%) larger than the experimental value (1.61 Å), in agreement with a general tendency of the GGA\(^{23}\). Using the same computational setup we found a similar overestimation in a preliminary test made on α-quartz. For the other peaks we found 3.18 Å for Si-Si and 2.68 Å for the O-O bond length.

From this analysis we concluded that our classical systems were well equilibrated. From the pair correlation functions we computed the static structure factor for the Car-Parrinello run which can be compared with experiments\(^{22}\). Experimentally the static structure factor can be obtained from neutron diffraction. In the simulations one possibility is to compute the static structure factor $S(q)$ by its relation to the pair correlation function $g(r)$:

$$S(q) = 1 + 4\pi \rho \int_0^\infty (g(r) - 1) \frac{\sin(qr)}{qr} r^2 dr \quad (2)$$

with

$$g(r) = \frac{\sum_{\alpha,\beta} c_\alpha b_\alpha c_\beta b_\beta g_{\alpha\beta}(r)}{\left[ \sum_{\alpha} c_\alpha b_\alpha \right]^2} \quad (3)$$

The integral in Eq. (2) has been evaluated by using the Filon’s method\(^{21}\). In equation (2) $\rho$ stands for the density. In Eq. (3) the $g_{\alpha\beta}(r)$ are the pair correlation functions ($\alpha, \beta = $ Si,O) while $c_\alpha$ and $b_\beta$ stand for the concentrations of the two species and $b_\alpha$ and $b_\beta$ are their scattering lengths. We chose $b_\alpha$ and $b_\beta$ to be 4.149 fm for Si and 5.803 fm for O. The integration from 0 to $\infty$ is performed as a summation from zero to half of the box size. The first sharp diffraction peak (FSDP) corresponds to 1.53 Å$^{-1}$ which is in good agreement with the experimental data (1.52 Å$^{-1}$)\(^{31}\). The other peaks are at 2.8, 5.19, and 7.83 Å$^{-1}$, respectively.

We finally studied the electronic density of states of
the system. We evaluated the Kohn-Sham density of states (Fig. 6). The density is in agreement with other DFT calculations. The calculated band gap is 5.7 eV and it is underestimated (experimental ∼ 9 eV) as usual in DFT due to the discontinuity of derivatives of the exchange-correlation functional. The DOS of amorphous and crystalline SiO$_2$ are very similar, because the short range order is similar for both structures. For this reason we can identify the states at about -20 eV as oxygen 2$s$ states, the states from -10 eV to -4 eV as bonding states between silicon $sp^3$ hybrids and oxygen 2$p$ orbitals and above -4 eV as oxygen 2$p$ nonbonding orbitals. The lowest conduction band are states with antibonding character.

VII. CONCLUSIONS

Using classical molecular dynamics and the BKS empirical potential we generated seven model systems of 72 atoms of a-SiO$_2$ at 300K. We further optimized the classical equilibrated configurations with plane wave based density functional theory and GGA approximation to the exchange correlation energy. In particular within ab initio treatment we showed that both geometry optimization and Car-Parrinello annealing applied to our systems lead to the same final configurations but the CPU time required for the geometry optimization to reach convergence is one fifth of the time needed by a Car-Parrinello annealing. The topology acquired by the amorphous silica model systems at the end of the classical quenching protocol did not change when treated in an ab initio way. The structural properties of the amorphous glass, like angle distributions, pair correlation functions, static neutron structure factor $S(q)$ and experimental results from neutron diffraction of normal and densified vitreous SiO$_2$ (from Ref. 31) (lower graph).
structure factor and electronic density of states have been accurately studied. The properties of rings in model systems have been accurately analyzed by energetical considerations. We found very similar results for both the description (classical and Car-Parrinello) and in good agreement with experimental data. The generated model systems will be used to study defects, and in particular the mechanism for bond weakening and electron localization in SiO₂.

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