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Molecular dynamics simulations of amorphous silica surface properties with truncated Coulomb interactions

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ABSTRACT

Molecular Dynamics simulations have been performed to evaluate the capacity of the van Beest, Kramer and van Santen (BKS) [1] potential with truncated Coulomb interactions as proposed by A. Carré et al. [2] to reproduce amorphous silica surface properties. We compare the results obtained with the truncated BKS potential with those obtained from its full-range interaction version. Energies of $(SiO_2)_n$ clusters are computed for both potentials. The energies and structural properties of small aggregates of silica (from ≈3.5 nm to 7.6 nm of diameter) are investigated at high temperature. Both potentials lead to the same results for those properties when considering the transition from the core to the shell of aggregates. The significant computation time saved with this cut-off on Coulomb interactions allows for large-scale simulations of silica aerogels.

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1. Introduction

Silica aerogels are highly nanoporous materials structured into a tortuous three-dimensional silica network. This high porosity can reach up to 99% with hypercritical drying [3]. Typically, 80% of the nano-size of pores is < 30 nm which is at the origin of their very low thermal conductivity [4]. These super-insulation properties come at the price of poor mechanical properties. Nevertheless, these materials are used in various applications such as heat barriers, insulation panels for buildings, microelectronics, optics and acoustic devices [5,6]. Many experimental [7–10] and modeling [11–14] studies cover various aspects of the mechanical behavior of this important class of materials. However there is still a lack of sound knowledge on the mechanical properties due to the multiscale nature of the porosity network and of the particles.

Molecular Dynamics (MD) is an atomistic simulation method well suited to study mechanical properties at nano-scale. However, the full investigation of a system is limited by the size (volume of material) and by the duration (CPU time) of simulations. It is even more valid for materials with ionic interactions such as silica. These materials need Coulombic interactions to be computed for long-range distances at a great cost in terms of computation time. Focusing on highly porous silica aerogels, most studies dealt with volumes of material smaller than 20^3 nm^3 [12,15,16,17]. Such small volumes are hardly representative of the whole structure. Campbell et al. [11] attempted a large-scale simulation (36^3 nm^3) with a density of 1670 $\mathrm{kg \cdot m^{-3}}$ (25% porosity) but it still leads to a low surface area compared to real aerogels. A recent study [18] dealing with thermal properties of silica aerogel exemplifies the constraints on MD simulations to reach realistic microstructures. Although the authors were able to reproduce successfully the power-law variation of thermal conductivity with density, they could not simulate samples with sufficiently large pores to compare directly with experimental observations. This is because several millions of atoms and systems with a length scale of hundred nanometers would have been required whereas <60.000 atoms were used in their study. Clearly, further progress in the simulation of silica areogels properties requires reliable potentials that allow for much larger MD simulations.

Concerning mechanical properties, a solution adopted by Ferreiro and Gelb [13,19] to get around the scaling problem consists in using Coarse-Grained Molecular Dynamics. Their model allows for the investigation of larger systems created with primary particles that interact through weak nonbonded forces and strong interparticle bonds. However the contact laws between primary particles during a simulated mechanical test need to be more realistic and accurate. Atomistic simulations that describe all interactions between atoms could advantageously be used as input for such Coarse-Grained simulations. In this context, the aim of our study is to demonstrate that using an effective interatomic potential in MD simulations, it is possible to simulate reasonably large volumes of material with high surface area.

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Various MD studies have focused on silica surfaces since the early eighties. Garofalini is one of the pioneer in this research area through his investigations on structure and diffusion of amorphous silica surface [20–23]. Garofalini has also investigated water adsorption with Mahadevan [24] and protonation of bridging oxygen sites with Lockwood [25]. In these two studies, a dissociative water potential with Wolf summation method has been used in order to truncate long-range Coulomb interactions. Ma et al. study [26] have discussed the convergence behavior of Wolf summation method. More recently, Rarivomanantsoa et al. [27] and Roder et al. [28] have investigated surface properties of thin silica film through MD simulations using the van Beest, Kramer and van Santen (BKS) potential [1]. The structures obtained with the BKS potential are close to those from *ab initio* calculations [29] that reveal the natural emergence of two-membered rings at the surface. Surface energies calculated by Roder et al. are also in good agreement with experimental values [30]. Mischler et al. [31] have compared in detail the structure of amorphous silica surfaces obtained with the BKS potential with *ab initio* molecular dynamics simulations using the Car-Parinello method (CPMD). They found a higher concentration of two-membered rings with the BKS potential as compared with the CPMD. For small scales (<5 Å), *ab initio* calculations are predictably more accurate for the simulation of the structure of silica surfaces. However, their results indicated that the structures obtained with both methods do not differ beyond 5 Å. When considering the need for an interatomic potential for silica [32] able to reproduce both bulk and surface properties of the amorphous phase at nano-scale, the BKS potential is a natural choice.

A recent study on silica bulk using BKS potential [33] showed that the contribution of long-range Coulomb interactions to the total energy is lower for the amorphous phase than for the crystalline phase at the same density. These recent results are in good agreement with the successful truncation of Coulomb interactions of BKS potential for amorphous phase [2]. This new potential truncated by Carré et al. [2] with Wolf shift method has been fitted on the original BKS potential to reproduce amorphous silica bulk properties. The benefits of this truncation compared to the computation of the full Ewald summation have already been discussed by Fennell et al. [34]. These authors have demonstrated that the results obtained with such a truncation method are in good agreement with those given by the full Ewald summation method for bulk systems. However, it is still an open question whether such a truncation is reliable for systems with free surfaces.

Here, we demonstrate that this new version of BKS without Coulomb long-range interactions [2] is able to reproduce the same silica surface properties as the original BKS potential. The significant saving in computation time could be used to study larger volumes of silica aerogels. All simulations have been performed with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [35].

2. Methods

2.1. Interatomic potentials

BKS is an empirical potential which includes a short-range contribution described by a Buckingham form and a long-range Coulombic contribution. It takes the general form for the interaction energy of atoms *i* and *j*:

$$\Phi_{BUCK}(r_{ij}) = a_{ij}\,exp(-b_{ij}r_{ij}) - \frac{c_{ij}}{r_{ij}^{6}}, r_{ij} \le r_{cb} \qquad (1)$$

$$\Phi_{BKS}(r_{ij}) = \frac{q_i q_j}{r_{ij}} + \Phi_{BUCK}(r_{ij}). \qquad (2)$$

where q_i is the effective charge, r_{ij} the interatomic distance and a_{ij}, b_{ij}, and c_{ij} are short-range parameters [1]. The cut-off, r_{cb}, for short-range interactions is 5.5 Å. The BKS potential pertains to the Coulomb-Buckingham and thus does not tend to positive infinity when r tends to zero. At very high temperature, atoms may approach too close from each other which may induce chaotic dynamics. A solution consists in adding a 24–6 Lennard-Jones potential which is strongly repulsive at short distance [16,36] to prevent overlapping atoms.

$$\Phi_{LJ}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{24} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], r_{ij} \le r_{cl} \qquad (3)$$

where r_{cl} is the cut-off radius of 3 Å and ε_{ij}, σ_{ij} parameters which can be found in Ng's study [16]. Since there is no cut-off on Coulombic term, all contributions are computed. This study involves free surfaces and no periodic boundary conditions, thus, the Coulombic term is computed using the Multilevel Summation Method (MSM) [37]. Also, when using periodic boundary conditions, the evaluation of the Coulombic term by the Ewald summation method [38] is the most CPU-time consuming stage for large systems. The long-range contribution of this type of potential (BKS) can be advantageously truncated. Carré et al. [2] used the Wolf shift method to introduce a finite distance cut-off on Coulomb interactions. The Coulombic term in Eq. (2) is approximated by $\Phi_W(r_{ij})$:

$$\Phi_W(r_{ij}) = q_i q_j\left[\frac{1}{r_{ij}} - \frac{1}{r_{cw}} + \left(\frac{1}{r_{cw}^{2}}\right)(r - r_{cw})\right], r_{ij} \le r_{cw} \qquad (4)$$

where r_{cw} is the cut-off on Coulomb interactions. The original Wolf shift is based on the screening of the charge contained in the cut-off sphere by placing an opposite charge on its surface. Eq. (4) is a modified version of Wolf shift method which has been proposed by Fennell et al. [34]. It ensures the continuity of both the potential and the forces at the cut-off radius, which was the main concern for the original Wolf shift. This Wolf shift method differs from the full Wolf summation used by Garofalini et al. [24,25] by applying a shift to the Coulomb interactions without damping electrostatic interactions. Fennell et al. [34] have shown very good agreement between this method and the full Ewald summation. Thus, Carré et al. [2] have applied this truncation on the BKS potential. Static and dynamic properties of bulk liquid silica such as the radial distribution functions, the bond angle distributions, the structure factor and the vibrational density of states have been fitted on silica bulk using periodic boundary conditions from the original BKS to its truncated version (denoted as Wolf BKS). This study uses a revisited version of the Wolf BKS potential with smoothed interactions and short-range repulsion (to prevent atoms overlapping at high temperature). Moreover, repulsive interactions between Silicon atoms have also been added compared to the original BKS. Those model improvements are meant to correct some known defects of the original BKS and to smooth interactions near the cut-off radius. They do not change significantly the properties of silica bulk. The full analytical expression can be found in Shcheblanov et al. [39].

2.2. Analysis of SiO_2 clusters using molecular statics

Molecular Statics is used to compute energies of small clusters (monomers, dimers, trimers and tetramers). Surface effects play an increasing role as the size of the system decreases. Thus, it is of interest to reproduce small silica clusters and investigate their total and binding energies to other MD results and to Density Functional Theory (DFT). In that case, atoms are initially located at coordinates given by Harkless et al. [40] and a potential energy minimization is performed using a conjugate gradient technique. The total and binding energies after minimization at 0 K are compared to energies from Harkless using the Tsuneyuki et al. (TTAM) empirical potential [41] which also computes Coulomb interactions.

A simple monomer (Fig. 1) with symmetric linear form $D_{\infty h}$ is first studied. It is composed by a silicon atom in between two oxygen

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