

Ab-Initio Molecular Dynamics Simulation of High Temperature GeO₂

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ABSTRACT. We made a series of molecular dynamic simulations to get a representative, high temperature GeO₂ system to eventually be quenched down to room temperature so as to obtain an amorphous system to be studied under pressure for comparison to experimental results. We carefully generated an initial configuration such that all simulations have entirely been carried out by ab-initio methods in the range 10K-3000K.

1 Introduction

The study of liquid and amorphous GeO₂ holds a particular interest among material sciences and physics researchers, due to the fact that GeO₂ presents many structural similarities with SiO₂ - short range order is the same - whilst undergoing phase transitions at much lower pressures. Moreover the differences between GeO₂ and SiO₂ glasses at the medium-range scale, allow glass transition temperature of GeO₂ to be considerably lower than for SiO₂. In addition, thanks to its higher electron and hole mobilities and its lower operating voltages, germanium is gaining increasing consideration for replacing silicon in solid state devices.

Due to currently available computational powers, molecular dynamics simulations are more and more often carried out to flank experimental results on Ge compounds.

On the base of the simulations we performed on a *numerical sample* made of Ge atoms [1, 2], we started a molecular dynamics study of GeO₂. As a preliminary step, our first goal was to get a representative GeO₂ system well over its melting temperature as a starting point to eventually obtain liquid and amorphous GeO₂ to be studied under external hydrostatic pressures.

In this paper we present the preliminary results obtained in simulating a system of 240 atoms, 160 oxygen and 80 germanium, at 3000K by first-principles molecular dynamics. First principles simulations require a suitable initial configuration, virtually at 0K, to be heated up to a target temperature through a series of equilibrated states at intermediate

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temperatures. It is known that the generation of initial configurations of GeO₂ to be gradually heated up is a delicate process; it is not unlikely to obtain a system for which the simulations diverge during the very first steps. This and the fact that first-principles simulations take long computation times to reach the temperatures of interest, are the reasons for which first-principles simulations are often started at high temperatures on initial configurations obtained by classical molecular dynamics methods [3].

Our approach has instead been to perform the entire simulation using ab-initio methods to get a liquid GeO₂ system at high temperature to be used as a starting system to obtain numerical samples of GeO₂, liquid and amorphous, to be characterized at the GeO₂ melting point (1389K) and at 300K, respectively.

2 Computational details

We considered for our system a density $\rho = 3.66 \text{ gr/cm}^3$, corresponding to the experimental density for GeO₂ in the temperature range of our interest [3], giving a cubic simulation cell edge of 1.56nm. To ensure that our final results were independent on the initial atomic positions, the starting configuration has been generated placing the atoms at random in the simulation cell imposing that mutual distances Ge-Ge, O-O, Ge-O were larger than certain suitable thresholds [4] (this procedure designs a highly defective starting configuration, well apart from the crystalline counterpart).

We further disordered the configuration by constant temperature and constant pressure MD equilibration at high temperature ($T = 3000\text{K}$), at which atoms covered a distance as long as about 2nm ensuring the final configuration retains no memory of the initial positions.

The software we used is CPMD (Car-Parrinello Molecular Dynamics) [5, 6].

The self consistent evolution of the electronic structure during the motion is described within density functional theory. A generalized gradient approximation (BLYP-GGA) has been adopted for the exchange and correlation part of the total energy [7, 8] and norm conserving pseudo-potentials have been used for the core-valence interactions.

A particular attention was paid to choose the cutoff value for plane waves; the electronic wave functions were expanded in plane waves up to a kinetic energy of 60Ry to get a low relative error on computed forces - the order of a few percent [9] - and shorter computation times while retaining a good computational accuracy.

After the initial wave function and geometry optimizations, the system was taken and equilibrated up to 10K, 50K, 100K,150K, 200K, respectively, and subsequently taken up to 3000K by steps of 100K. An integration time step of 3a.u. (0.072fs) was used for the initial optimizations, whereas a time step of 5a.u. (0.12fs) was used at all temperatures for a total simulation in temperature 50ps long (24ps of which at 3000K).

During the equilibration of the system at each intermediate stage a Nosè thermostat was used for each degree of freedom to control the ions temperature [10, 11, 12]. The characteristic frequency for the thermostat was 1000cm^{-1} . A second Nosè thermostat

was used to control the fictitious electronic kinetic energy. This thermostat prevents the electronic wave functions from drifting away from the instantaneous ground state (the Born-Oppenheimer surface), by removing excess fictitious kinetic energy. This drift is particularly large for metals. The characteristic frequency for the electrons thermostat was 10000cm^{-1} and the target kinetic energy was chosen according to [13]. The Nosé thermostat on the electrons was used throughout the simulation and proved to be an effective way of keeping the electrons on the Born-Oppenheimer surface.

3 Computational resources

Fig. 1 shows the pair distribution function for the final GeO_2 system at 3000K after a 24ps long equilibration. As expected, the atoms has undergone relatively large displacements and the new configuration is well apart from the initial one: the final geometry correctly shows the typical mutual distances O-O, Ge-Ge, Ge-O reported for GeO_2 systems at the same temperature [4].

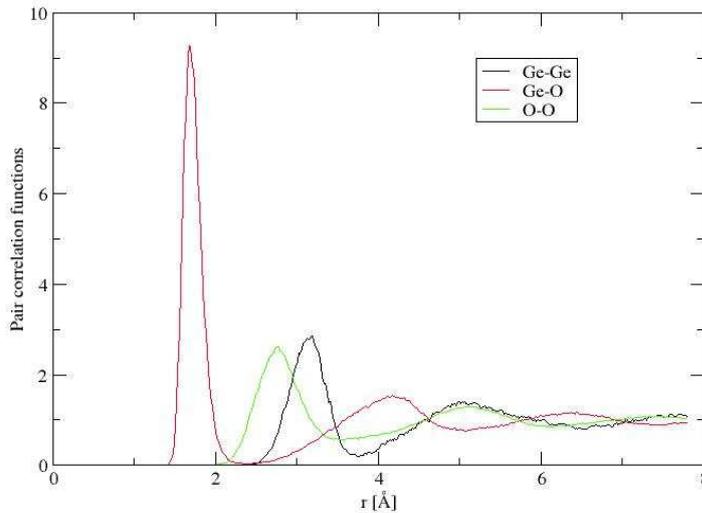


Figure 1: Radial distribution function from the simulated GeO_2 system at 3000K.

We can then conclude that we actually have obtained a reliable GeO_2 system at high temperature by first-principles molecular dynamics. Starting from this very result, the evolution of our system when taken down to 1389K is currently being computed; the additional results will hopefully be object of future communications.

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