MOLECULAR DYNAMICS OF GeO_2: CAR-PARRINELLO SIMULATIONS IN THE RANGE 10-4000 K

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ABSTRACT. First-principles molecular dynamics simulations have been carried out for a relatively large system consisting of 240 GeO_2 atoms at 4000 K. We have finally covered the range 3000-4000 K, completing a long simulations process aimed to obtain a high temperature GeO_2 system entirely by ab-initio simulations in the whole range 10-4000 K.

1 Introduction

In this paper we present the results and details of our ab-initio Car-Parrinello (CPMD) simulations [1,2] of a system formed by 240 atoms, 160 oxygen and 80 germanium – a relatively large system for first principles simulations - at 4000 K.
We consider these results the last step of a series of first-principles simulations carried out to prepare a numerical sample of liquid GeO_2 at high temperature to start production runs, from which distinct amorphous GeO_2 configurations at room temperature can be obtained and studied.
First principles simulations take their very start from a suitable initial configuration, virtually at 0 K, to be taken up to a target temperature through a series of intermediate, equilibrated states. The generation of the initial configurations of GeO_2 to get stable simulations can result into a long, delicate process; in fact, simulations often diverge after a few steps. This fact and the short timescales provided by first-principles simulations are the reasons for which first-principles simulations are often started on initial high temperatures configurations obtained by classical molecular dynamics methods. We here stress the fact that we have covered the entire temperature interval 10-4000 K using ab-initio methods.
It is experimentally known that the activation energy of the structural relaxation time for GeO_2 is about 3.4 eV; at a temperature of 3000 K this time is longer than 100 ps. Due to the intrinsic limitations arising from the shorter typical timescales of ab-initio simulations – namely CPMD in our case - a temperature of 3000 K has to be considered as the lowest one to carry out production CPMD simulations, provided smaller systems and shorter times than classical molecular dynamics are considered [3].
We have reported the results of our 24 ps-long CPMD simulations at 3000 K in [4]. In that paper a comparison of the results obtained from different simulation parameter considerably affecting the computing times has been presented, showing no significative differences. As a matter of facts, our preferred approach was in favour of the fastest runs; nevertheless we flanked them by longer and potentially more accurate simulations so as to ascertain that the results only depended on the sole configuration of our system.

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To reach the final 4000 K temperature, characterised by a faster dynamic during production runs, we only continued with the most demanding approach in terms of computational times - the one using a plane wave cut-off of 90 Ry - for easier, more homogeneous results comparison.

2 Computational details

We started from a well equilibrated GeO_2 system at 3000 K consisting of 240 atoms in a cubic simulation box of edge 15.602 Å, corresponding to a density ρ= 3.66 gr/cm^3 [4]. The software we used is CPMD (Car-Parrinello Molecular Dynamics [1,2]).
The self consistent evolution of the electronic structure during the motion is described within the density functional theory. A generalized gradient approximation (BLYP-GGA) has been adopted for the exchange and correlation parts of the total energy [5,6]. For the core-valence interactions, norm conserving pseudo-potentials with the BLYP exchange–correlation functional using the Troullier–Martins parametrization [7] has been chosen.
Car-Parrinello molecular dynamics simulations have been carried out on the system heated up and equilibrated from 3000 to 4000 K by steps of 200 K.
For faster equipartioning, a "massive" thermostatting has been used for the ions (a Nosé-Hoover chain thermostat placed on each ionic degree of freedom [2,8,9]). A second Nosé-Hoover chain thermostat has been set on the electronic degrees of freedom to prevent electrons from provoking improper ions damping or departures from the Born-Oppenheimer surface. Thermostats have been systematically employed throughout all simulations; characteristic frequencies of 1000 cm^{-1} for ions and 10000 cm^{-1} for electrons have been used. The default value of 400 a.u. has been used for the fictitious electronic mass. A plane wave cut-off of 90 Ry and a time step of 3 a.u. have ben used during all simulations.

3 Computational resources

The calculations were performed using the facilities and services available at the ENEA GRID infrastructure (Italy). Molecular Dynamics simulations have been carried out using CPMD v3.15.3 running on CRESCO4 cluster. 800 GB of disk storage has been granted on the PFS/gporq1_256k file system.

4 Results and conclusions

As expected, in its final state at 4000 K the system shows broader distributions than at 3000 K, still retaining the same central values. Figs. 1-3 clearly show this behaviour.
From our simulations we have for the positions of the first $g_{\alpha\beta}(r)$ peaks (fig.1): 3.12 Å for Ge-Ge, 1.69 Å for Ge-O and 2.75 Å for O-O distances, respectively. They are in perfect agreement with the values from other mixed classical/ab-initio simulations, e.g. [10], and in good agreement with classical MD and experimental results [10,11,12], the slight variations are commonly attributed to the different system preparation procedures (we are considering the possibility of repeating the whole set of simulations on a different initial GeO_2 configuration than presented here, so as to verify this point).

Similar considerations apply for the average coordination numbers (fig.2): our simulations give Z_{GeGe}=4.1, Z_{GeO}=4.0 and Z_{OO}=6.8 (all values are taken at the intersection points of the 4000 K and 3000 K curves: it seems particularly reasonable for Z_{OO}, since the associate distribution curves show no clearly defined plateau). Finally fig.3 gives the initial an final structure factors: it's easily seen how they too are in good agreement with the ones reported in literature.
We can thus conclude we actually have obtained a reliable, relatively large liquid GeO_2 system at high temperature entirely in the frame of first-principles molecular dynamics. The system will be used for production runs to obtain amorphous GeO_2 systems to be studied at room temperature.

The resources available at HPC CRESCO systems make CPMD simulations using Goedecker pseudo-potentials [13] – commonly considered out of reach a target when dealing with a significant number of atoms - a feasible goal. Such pseudo-potentials are analytical - that ensures their separability - and have no "ghost states", but they generally need higher plane wave cut-offs (100-200 Ry) than the corresponding Troullier-Martins ones.
We have started new simulations - on the same initial GeO_2 configuration we have presented in this paper - using Goedecker pseudo-potentials with 100 and 200 Ry cut-offs, so as to evaluate the differences, if any, due to distinct potentials. The results will be a subject of future communications as soon as they are obtained.

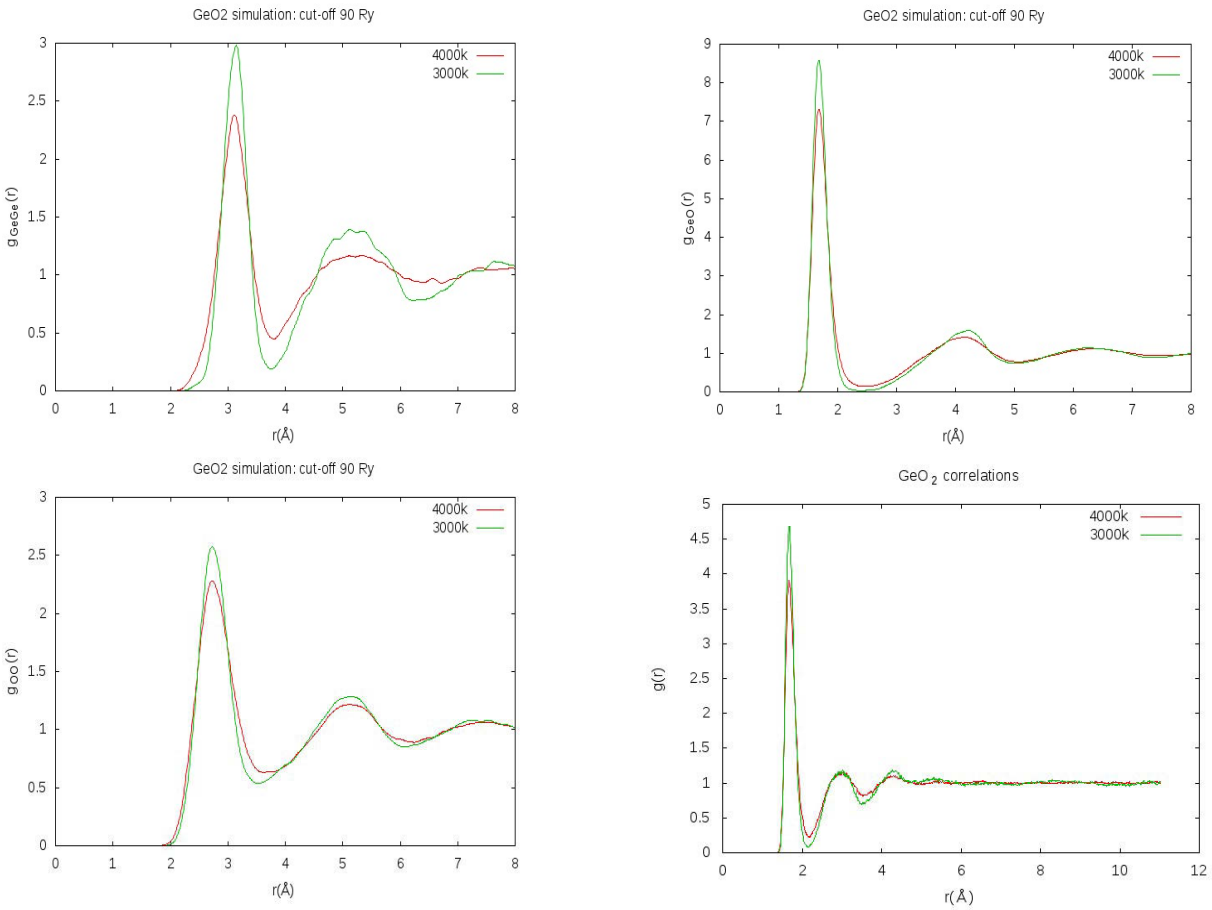

Fig.1: Radial distribution functions from the simulated GeO_2 system at 3000K and 4000K.

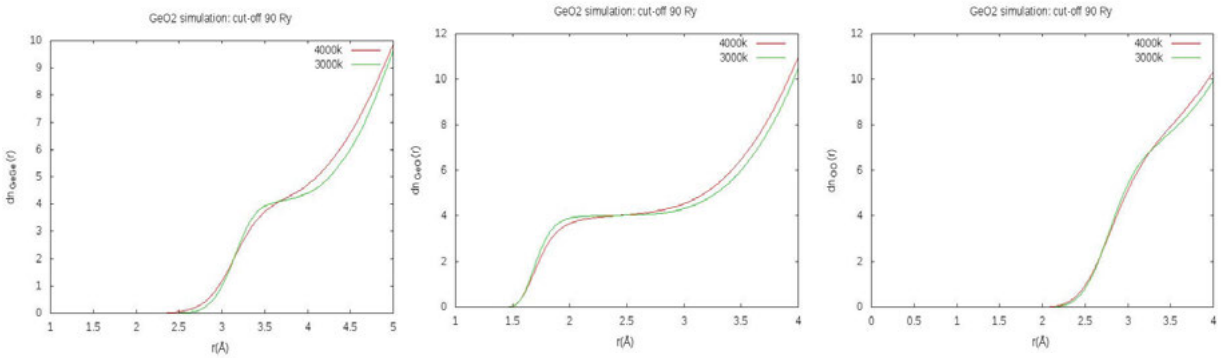

Fig.**2**: $Z_{\alpha\beta}(r)$ distribution from the simulated GeO_2 system at 3000K and 4000K.

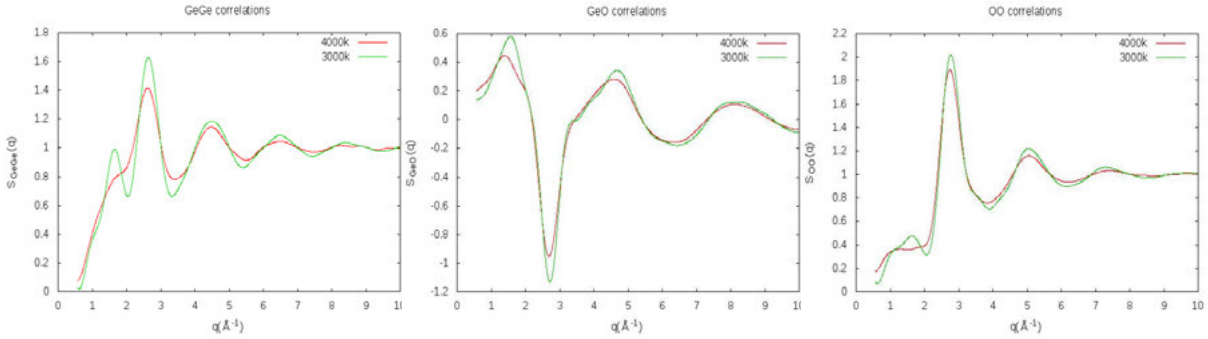

Fig.3: $S_{\alpha\beta}(q)$ structure factors from the simulated GeO_2 system at 3000K and 4000K.

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