

DEPENDENCE ON PSEUDOPOTENTIALS OF AB-INITIO MOLECULAR DYNAMICS SIMULATIONS OF HIGH TEMPERATURE GeO_2

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ABSTRACT. Two series of *first-principles* molecular dynamics simulations have been carried out in the framework of the density functional theory on a large system consisting of 240 GeO_2 atoms. The entire temperature range 10-4000K has been covered by *ab-initio* simulations on the same initial configuration using two different norm conserving pseudopotentials with the BLYP exchange-correlation functional. The results are compared with experimental data.

1 Introduction

Thanks to its higher electron and hole mobilities together with its lower operating voltages, germanium is gaining increasing consideration to become a material of election for the production of less energy-demanding solid state devices. As a consequence, the interest for further investigations of its properties has recently been renewed by many scientists. In this context molecular dynamics (MD) simulations have firmly become a valuable means to flank, and possibly integrate, experimental results. The possibility to get information that are difficult, if not practically impossible to access by direct experimental measurements, calls for effective reliability of MD simulations. The computing power available nowadays makes it possible to implement more sophisticated models to run on larger systems than just a few years ago, allowing for richer, more detailed and accurate results; *first-principles* or *ab-initio* MD is credited with being an important step in this direction. Nevertheless, thorough comparisons of MD results with experimental data are of primary importance, since the simulations can be trusted for additional information only if known quantities are correctly reproduced. In the present paper we illustrate the results we have obtained by *ab-initio* MD simulations carried out using the Car-Parrinello Molecular Dynamics software (CPMD) [1, 2, 3] to study the properties of GeO_2 . The CPMD approach, based on the density functional theory, uses plane waves and pseudopotentials to represent valence and core electrons, thus the choice of functionals, plane waves cut-offs, pseudopotentials and integration timesteps, has an important impact on computational times, hardware resources and, of course, on results. In a preceding paper [4] we presented a comparison of CPMD simulations for GeO_2 at 3000K carried out using different kinetic energy cut-offs for plane waves expansions, showing that an appropriate choice (60 Ry in our case, allowing for a 10a.u. timestep) gives the same results on shorter runs, less processors and memory than the commonly suggested higher values (80-90Ry, 3a.u. timestep). Anyway, for

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ease of comparison with other authors, we continued with the only 90Ry cut-off to reach 4000K [5]. As for the functionals and pseudopotentials, we adopted norm conserving pseudopotentials with the BLYP exchange-correlation functional using the TroullierMartins parametrization in the Kleinman-Bylander separable form for the core-valence interactions [6]. Our simulations, entirely carried in the *first-principles* frame constituted by CPMD, gave the the positions of the first $g_{\alpha\beta}(r)$ shown in the second column of Table 1 [5]. These values are in perfect agreement with the ones obtained by mixed classical/*ab-initio* simulations, e.g. [7], and in good agreement with classical MD and experimental results [8, 9]. When using the same pseudopotentials, the slight differences with experimental data are commonly attributed to the differences in the initial configurations and preparations. It is worth noticing that a long enough equilibration at higher temperatures than the melting point should lead the system to retain no memory of the initial conditions, so that – it was our opinion – the subsequent outcomes only depend on pseudopotentials. We have verified this point repeating the entire set of *ab-initio* simulations on the same initial GeO₂ configuration using separable, dual-space gaussian pseudopotentials due to Goedecker et al. [10], so as to check for correspondence, if any, of the results from distinct potentials. Pseudopotential(s) due to Trullier-Martins and Goedecker will be respectively indicated as T-M and GOE from now on.

2 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. 800GB of disk storage has been granted on the PFS/gporq1_256k file system.

3 Simulations details

A second cycle of CPMD simulations was performed on the same initial GeO₂ system we started from previously [4]: 240 atoms positioned at random in a cubic simulation box of edge 15.602Å to give a density $\rho = 3.66 \text{ gr/cm}^3$. Apart from switching from T-M to GOE and setting a higher kinetic energy cut-off (actually set at 100Ry) required by GOE for plane-waves expansion, we left the other parameters untouched: BLYP-GGA generalized gradient approximation for the exchange and correlation parts of the total energy, 400a.u. for the fictitious electronic mass, 1000cm⁻¹ and 10000cm⁻¹ for the characteristic frequencies of ions and electrons, respectively, and 3a.u. for the timestep. After initial plane-waves and geometry optimisations, Car-Parrinello molecular dynamics simulations were carried out on the system heated up from 10K to 4000K by steps of 200K using a massive thermostating for the ions (a Nosé-Hoover chain thermostat placed on each ionic degree of freedom [3, 11, 12]). A second Nosé-Hoover chain thermostat was set on the electronic degrees of freedom to prevent electrons from provoking improper ions damping or leaving the Born-Oppenheimer surface. GOE constantly demanded 40% longer execution times than T-M at 90Ry did during all simulations. At 4000K, as we did for M-T, we allowed for a long, final equilibration through 600,000 time steps (3 a.u. each one), amounting to 44ps. The determination of the appropriate cut-off value of 100Ry was performed in the same way we chose it for T-M, strictly abiding by the prescriptions given in the CPMD user’s manual for such a choice. Nevertheless, just for pure curiosity, we timed some executions times for GOE at 150Ry on CRESCO4 cluster: they were 280% longer than T-M.

4 Results

Liquid GeO_2 at 4000K, well over the melting point, presents wider, lower first peaks for $g_{\alpha\beta}(r)$ than at 300K, but their positions are expected to remain the same if cooled down to 300K. The results we present here are shown against the experimental data measured at 300K (as a matter of fact, for ease of comparison, we digitalized an experimental data curve by hand, so it results noisy with respect to the more accurate curves in [8, 9]). As shown in Fig.1 and Table 1, the Goedecker pseudopotentials

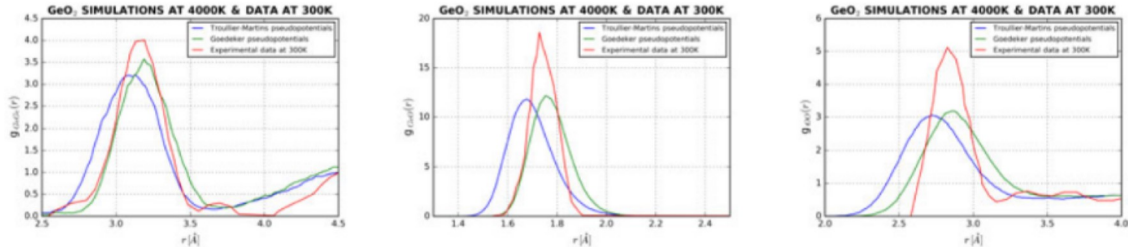


Figure 1: Pair distribution functions from simulations and experimental data

led to evident different results than the Troullier-Martins ones; in particular all interatomic distances by GOE are longer than T-M, and closer to experimental values. We showed that Troullier-Martins pseudopotential for germanium gave very accurate results when compared to experimental data [13, 14, 15], so it seems reasonable to attribute the different results for GeO_2 to the MT pseudopotential for the oxygen: an hypothesis still to be thoroughly investigated, but strenghten at the moment by the fact that the largest displacement in the first $g_{\alpha\beta}(r)$ peaks is due to the oxygen and amounts to three times the other ones [Table 1].

Table 1: Positions of the first $g_{\alpha\beta}(r)$ peaks and coordination numbers from Troullier-Martins and Goedecker pseudopotentials

	Troullier-Martins@4000K	Goedecker@4000K	Experimental@300K
r_{GeGe}	3.12 Å	3.18 Å	3.16 Å
r_{GeO}	1.69 Å	1.75 Å	1.73 Å
r_{OO}	2.75 Å	2.86 Å	2.83 Å
z_{GeGe}	4.1	4.1	4.1
z_{GeO}	4.0	4.0	3.8
z_{OO}	6.9	6.9	6.7

A series of short simulations (labelled GOE→T-M for short) imposing M-T potentials to the results from GOE, showed the higher mobility of the first peaks of $g_{GeO}(r)$ and $g_{OO}(r)$ that moved to the M-T positions. A smaller displacement was observed for $g_{GeGe}(r)$, probably due to the short simulation time [Fig.2]. All GOE→T-M pair distribution functions showed lower and wider peaks than both GOE and T-M. Similar considerations applied to the structural properties, as shown in Fig.3 comparing the results for the static structure factors $S_{\alpha\beta}(q)$ and $S(q)$ from GOE, T-M and GOE→T-M simulations.

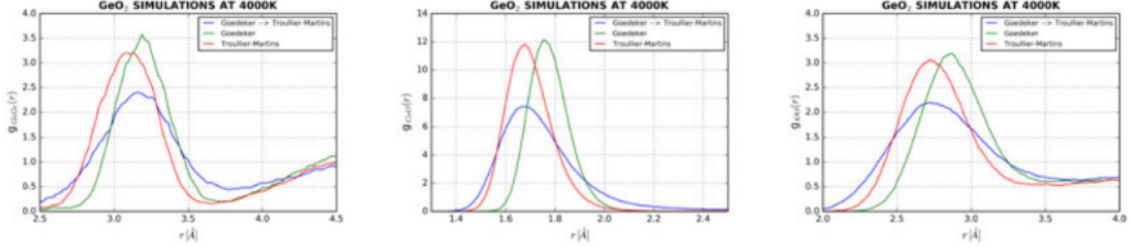


Figure 2: Pair distribution functions from original and crossed GOE→T-M pseudopotentials

As for coordination numbers, both approaches gave the same results [Table 1] (the data - not reported here - clearly showed for GOE the same plateaux as M-T, just shifted towards shorter distances).

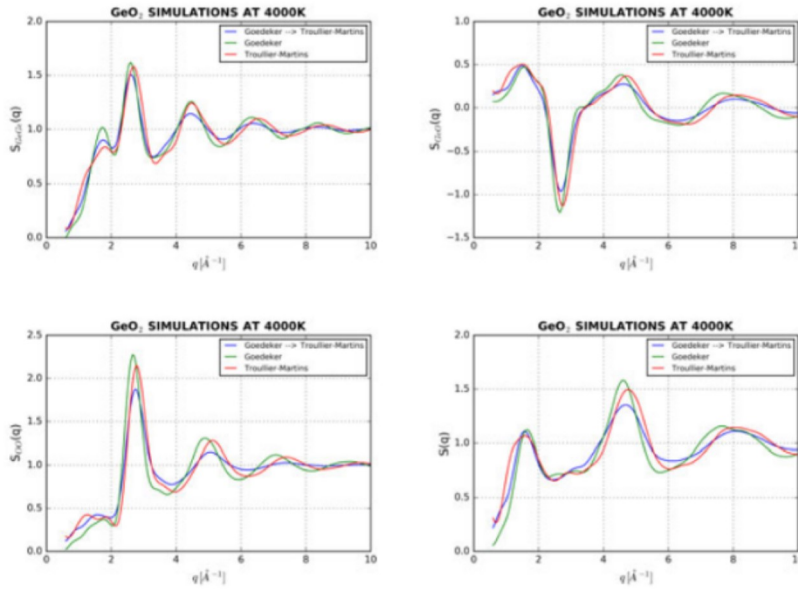


Figure 3: Structure factors from original and crossed GOE→T-M pseudopotentials

5 Conclusions

Troullier-Martins pseudopotentials led to shorter distances than experimental ones both when used through the entire 10-4000 K simulations range and when cross-applied to the wider distanced configuration resulting from Goedecker pseudopotentials at 4000K . In this last aspect, we somewhat imitate the mixed approach consisting in using classical MD results as starting points for *first-principles* simulations, showing that even a short simulation evolved to the same shorter distances than experimental ones as reported in [5, 7], making it impossible for us to reproduce the results shown in [8] although they too were obtained from wider starting configurations at high temperature, using the same software (CPMD). The results we have presented clearly show that *first-principles* CPMD simulations of high temperature GeO₂ using Goedecker pseudopotentials led to improved results with respect to Troullier-Martins ones. The positions of the first peaks of the pair distribution functions closely reproduced the

experimental values. This result is expected to remain as such when the system will be quenched back down to room temperature to finally get an amorphous GeO₂ sample.

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