Ab Initio Carr-Parrinello Simulations of High Temperature GeO_2: a comparison of the effects of plane waves cut-off and time step choice.

Giorgio Mancini[1*] and Massimo Celino[2]

[1]*Università di Camerino, sezione di Fisica della Scuola di Scienze e Tecnologie, Via Madonna delle Carceri 62032, Camerino (MC), Italy*

[2]*ENEA, Ente per le Nuove Tecnologie, l'Energia e lo Sviluppo Economico Sostenibile C. R. Casaccia, Via Anguillarese 301, 00123 Roma, Italy*

ABSTRACT. Ab initio Carr-Parrinello simulations of high temperature GeO_2 have been carried out using a set of different parameters supposedly significantly affecting the results, as well as the computing times. A particular attention has been paid to the effects related with the plane waves cut-off using lower and higher values than commonly suggested. Comparisons of the results for the different values are presented and illustrated indicating that the results are essentially the same.

1 Introduction

We have recently presented the preliminary results of the simulations of a 240 atoms, high temperature GeO_2 system, entirely carried out by *ab initio* (AI) molecular dinamics (MD) simulations using the CPMD (Carr-Parrinello Molecular Dynamics) software [1]: an approach distinct from the ones consisting in using classical molecular dynamics (CMD) results for GeO_2 at much higher temperatures (4000-7000K) as starting configurations for AI simulations to be carried out at lower final temperatures [2]. The main reason to adopt such a hybrid approach is that it allows to bypass both the limitations due to the short time scale accessible from *ab initio* simulations and the usually long, delicate, often unsuccessful process needed to prepare a "stable" system to start with (CPMD simulations on unstable systems abruptly diverge even from the very first runs at temperatures as low as 10~50K).

As for the computation times required by *ab initio* simulations, once the general frame in which they are carried out is set (let's simplistic say, once functionals and pseudo-potentials are chosen), they only depend on the values used for both the time step and the kinetic energy cut-off for electronic plane waves expansion: they must respectively be taken to be short and high enough to allow for meaningful, correct simulations; but shorter time steps and higher cut-offs mean longer computational times and/or larger computational resources.

In the results we have previously presented for GeO_2 [3], strictly abiding by the prescriptions given in the CPMD user's manual for such a choice [4], we have used a time step of 5 a.u (~0.121 fs) and a value of 60 Ry for the plane waves cut-off: respectively a higher and a lower value than the ones commonly suggested and used in literature (3 a.u. and 70-75 Ry) [1, 5].

To evaluate the extent of the possible differences on the results as a consequence of a more demanding choice of such parameters, we have carried out two additional CPMD simulations series to obtain high temperature GeO_2 using higher cut-offs values (80 and 90 Ry) on the same initial system we previously studied.

*Corresponding author. E-mail: giorgio.mancini@unicam.it

2 Computational resources

The calculations have been performed by using the facilities and services available at the ENEA GRID infrastructure (Italy). Molecular Dynamics simulations have been carried out using CPMD v3.15.1 on CRESCO4 cluster, using 512 processors per run, 400 GB of disk storage has been granted on the PFS/porq1_1M file system.

3 Computational details

We have performed three separated series of Carr-Parrinello, first-principles simulations on a GeO_2 system consisting of 240 atoms; the series correspond to kinetic energy cut-off values for plane waves expansion of 60, 80 and 90 Ry, respectively. The initial GeO_2 configuration to start the simulations on has been generated placing 80 germanium and 160 oxygen atoms at random in a cubic simulation box of linear dimensions L=15.602 angstroms, corresponding to a density $\rho = 3.66$ gr/cm^3; the only condition imposed has been their distances being larger than certain suitable values [3].
To perform CPMD simulations, we have adopted the generalized gradient approximation (GGA) for the exchange and correlation part of the total energy and norm conserving pseudo-potentials with the BLYP exchange–correlation functional using the Troullier–Martins parametrization for the core-valence interactions.
We have run the wave-function optimization processes imposing that the wave-functions be converged very well by setting a very strict convergence criterion ($GEMAX < 10^{-13}$) [4]. The subsequent geometry optimizations too have been performed setting a stricter convergence criterion than usual ($GNMAX < 10^{-6}$) [4]. An integration time step of 3 a.u. (0.072fs) has been used for the initial optimizations. After wave function and geometry optimizations, Carr-Parrinello molecular dynamics simulations have been carried out on the systems heated up and equilibrated at 10K, 50K, 100K,150K, 200K, respectively, and up to 3000K by steps of 100K.
To allow for shorter equilibration times, "massive" thermostatting has been used for the ions (a Nosé-Hoover chain thermostat placed on each ionic degree of freedom). A second Nosé-Hoover chain thermostat has been set on the electronic degrees of freedom to keep electrons on the Born-Oppenheimer surface throughout all MD simulations. Characteristic thermostats frequency 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.
The integration time step of 5 a.u. (0.12fs) used on the entire temperature range for the 60 Ry cut-off have turn out to be too long for the higher cut-offs since the very beginning (the simulations at 5K have diverged after a few steps). We are not able to tell whether this is a generalized behaviour or not, but we systematically have experienced it on several configurations. Consequently a time step of 3 a.u. has been used for the 80 and 90 Ry (this turned out to be the longest possible time step at all temperatures for us to have stable simulations).
On a computer equipped with SD hard disks, 64 GB ram (much larger than effectively used) and a last generation Intel I7 on which CPMD runs on twelve almost perfectly balanced parallel threads, the required time per single step of CPMD has dramatically grown when switched from 60 Ry to 80 or 90 Ry. On the contrary, when run on CRESCO4 cluster batch queues, 512 cpu's have proved sufficient to obtain the same computation times per single CPMD step for all the cut-offs values. As a matter of facts, on the I7, the required times for 80 and 90 Ry where practically the same and approximately three times those for 60 Ry; on the other hand, the simulations for 60 and 90 Ry have run about ten and thirty times faster on CRESCO4 than on I7. In conclusion, the simulation pro-

cesses times have depended only on the time step; the higher cut-offs requiring a time almost twice longer than for 60 Ry: a ratio not to neglect when it comes to *ab initio* simulations.

4 Results and conclusions.

It is important to notice how the geometry optimization processes have determined different initial positions for the three systems, so that they have undergone independent, separate evolutions in time and temperature from the very beginning. Since the simulations have begun at different times, we have compared them in the common time interval they have covered: a total time of 36 ps, 16 ps of which spent at 3000K.
The results of the simulations are depicted in figs. 1-3, showing radial distribution and static structure functions. Similar, almost superposing, results hold for dn(r), angles and bonds distributions.

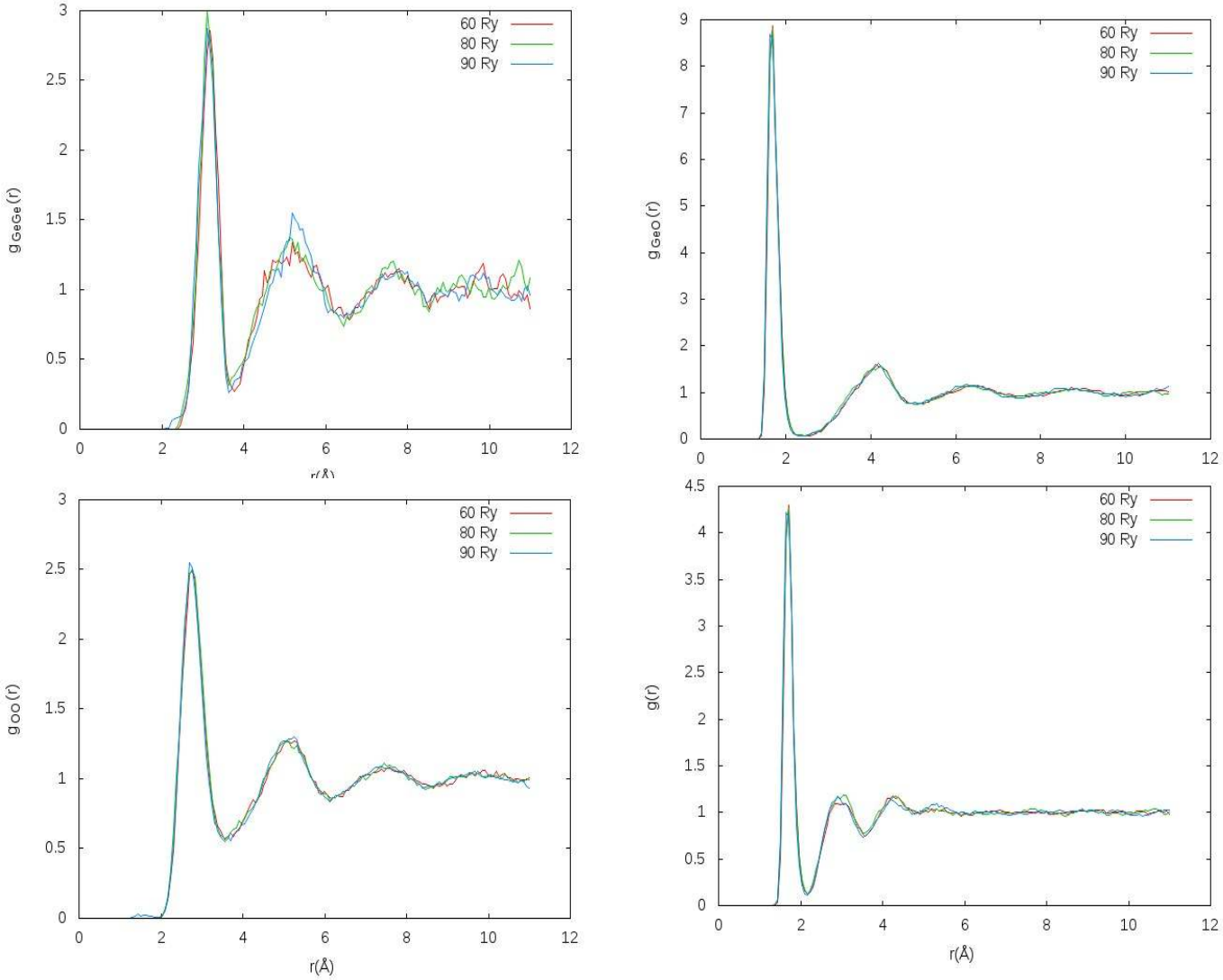

Fig. 1: Partial and total radial distribution functions for cut-offs 60, 80 and 90 Ry.

The simulations have essentially led to the same results for all relevant properties, thus validating the choice of using lower wave-function expansions cut-off for shorter simulations times to get the maximum possible efficiency while maintaining accuracy.

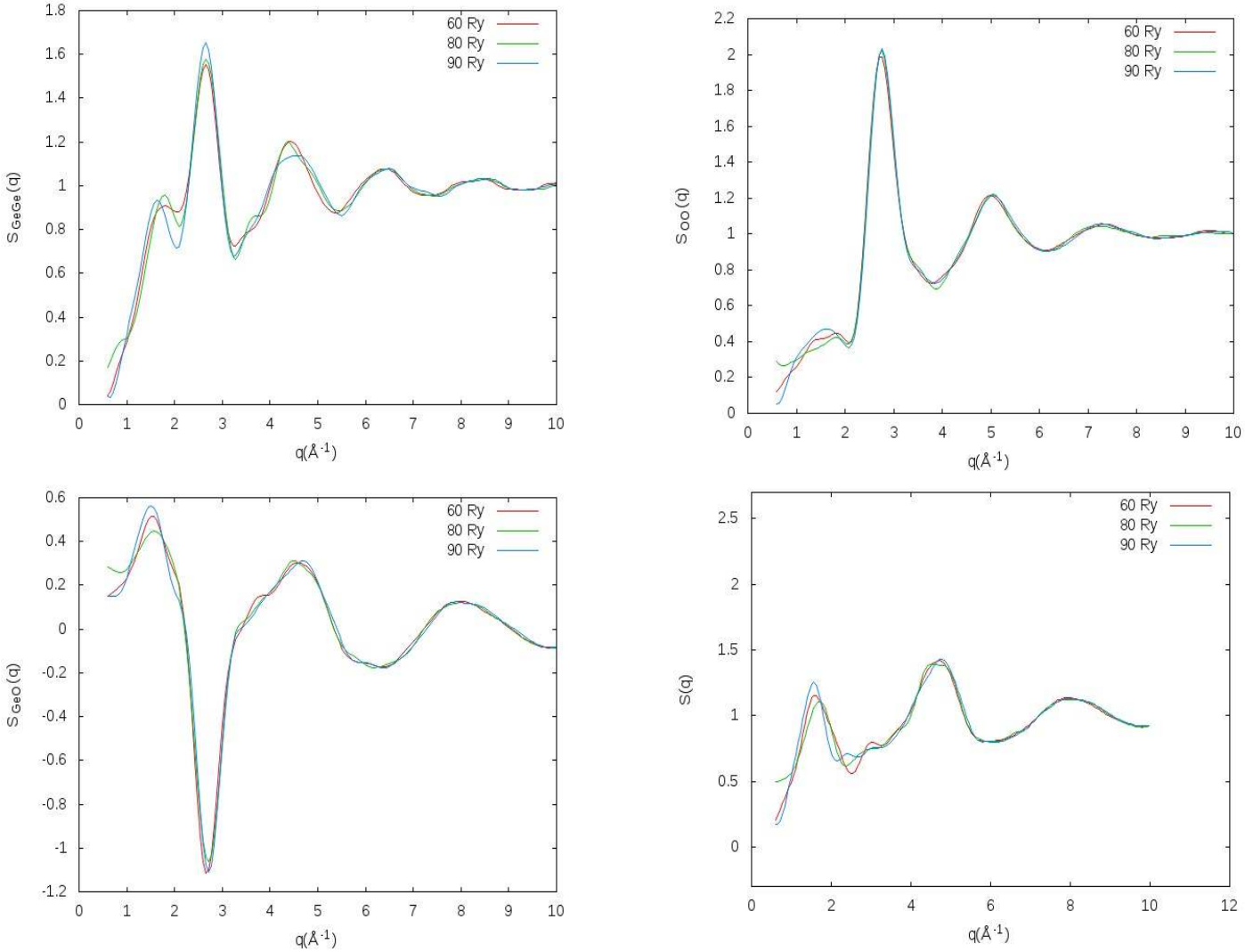

Fig. 2: Partial and total static structure functions for cut-offs 60, 80 and 90 Ry.

References

[1] CPMD, *Copyright IBM Corp 1990-2008, Copyright MPI für Festkörperforschung Stuttgart 1997-2001.*

[2] M. Hawlitzky, J. Horbach, S. Ispas, M. Krack, and K. Binder. *"Comparative classical and ab initio molecular dynamics study of molten and glassy germanium dioxide"*. J. Phys. Condens. Matter **20** (2008) 285106 (15pp)

[3] G Mancini, M. Celino, and A. Di Cicco. "*Ab-Initio Molecular Dynamics Simulation of High Temperature GeO_2*". High Performance Computing on CRESCO infrastructure: research activities and results 2014, ISBN: 978-88-8286-325-8 (2015) pp. 46-49.

[4] The CPMD Consortium. "*Car-Parrinello Molecular Dynamics: An ab initio Electronic Structure and Molecular Dynamics Program. Manual for CPMD, version 3.15.1*".

[5] Peter Broqvist, Jan Felix Binder, Alfredo Pasquarello. "*Atomistic model structure of the Ge(100)–GeO_2 interface"*. Microelectronic Engineering **86** (2009) pp. 1589–1591,