Large scale molecular dynamics simulations of phase change materials

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ABSTRACT

We present results of large scale (4000 atoms) atomistic simulations of liquid and amorphous GeTe based on a classical interatomic potential obtained by fitting a huge database of ab-initio energies by means of a Neural Network method. The availability of a reliable classical potential will allow addressing several issues on the properties of phase change materials presently beyond the capability of density functional based simulations.

Key words: ab-initio simulations, molecular dynamics simulations

1. INTRODUCTION

In the last few years atomistic simulations based on density functional theory have provided useful insights on the properties of phase change materials (see ref. [1] for a review and [2,3] for our results). However, several key issues such as the crystallization dynamics, the properties of the crystalline/amorphous interface and the thermal conductivity at the nanoscale, just to name a few, are presently beyond the reach of fully ab-initio simulations.
A route to overcome the limitations in system size and time scale of ab-initio molecular dynamics is the development of classical interatomic potentials. Traditional approaches based on the fitting of simple functional forms turned out to be unfeasible due to the complexity and variability of the chemical bonding in the crystal and amorphous phases revealed by the ab-initio simulations [2,3]. A possible solution has been devised recently by Behler and Parrinello [4] who developed empirical interatomic potentials with close to ab-initio accuracy for elemental carbon, silicon and sodium by fitting large ab-initio database within a neural network (NN) scheme. In general, a NN method is a non-linear technique that allows fitting any function to arbitrary accuracy and does not require any knowledge about the functional form of the underlying problem. By means of this technique, we have developed a classical interatomic potential for GeTe which is one of the compounds under scrutiny for applications in phase change memories. We here discuss the validation of the potential by comparing results on the structural and dynamical properties of liquid, amorphous and crystalline GeTe obtained from classical and fully ab-initio simulations.

2. COMPUTATIONAL DETAILS

Artificial NNs, biology-inspired machine learning algorithms, are emerging as a new class of interatomic potentials that combine the accuracy of an ab initio description of Potential Energy Surfaces (PES) with the efficiency of empirical force fields [4-6]. The PES is represented by a highly flexible NN capable of describing various bonding patterns in the system. Given a number of atomic configurations for which the ab initio energies are known the NN is tuned to reproduce these energies in the training process. Overfitting, i.e. obtaining a good fit to the training data, but performing less accurately when making predictions, is controlled by testing the performance of the NN for an independent test set not used in the optimization. Once trained, the NN performs interpolation to reconstruct the potential energy for new atomic configurations with the speed of empirical potentials and is, thus, useful to perform long molecular dynamics runs for large systems. The NN methodology overcomes many problems associated with empirical potentials. First and foremost, NNs completely obviate the problem of guessing a complicated functional

form for the energy in terms of atomic positions. This form is determined automatically by the NN. Second, the entire training procedure is fully automated so that NNs can be readily extended to new regions of the PES. Finally, the accurate mapping of ab initio energies ensures that all properties determined by the topology of the PES are described with the accuracy comparable with that of first principles calculations. In the past decade NN potentials have been constructed for a variety of systems [6]. Until recently, the main limitation of most NN approaches has been the small number of degrees of freedom that could be described which confined their application to small molecules. This limitation has been overcome by Behler and Parrinello who introduced a NN potential in which the total energy is expressed as a sum of atomic energy contributions depending on the local environments [4]. In this approach the energy contribution of each atom is evaluated using an individual NN instead of using one NN for the total energy of the system. The accuracy of this potential, which is applicable to systems containing thousands of atoms, has been demonstrated by reproducing the high-pressure phase diagram of silicon, carbon, and sodium [4]. This scheme has been recently extended to binary systems by including long range coulomb interaction between environment dependent ionic charges [5]. In the case of GeTe, we are faced with the problem of developing a potential suitable to describe both the semiconducting crystalline and amorphous phases as well as the metallic liquid. Therefore we decided to neglect long range coulomb interactions and to develop a short range NN potential.

In the NN scheme, the atomic energies are calculated by a standard feedforward NN as a function of the energetically relevant geometric environments of each atom which is described by several local order parameters called symmetry functions. The symmetry functions include radial and angular many-body terms and depend on the positions of all neighbours within a specified cut-off radius. The use of symmetry functions, instead of Cartesian coordinates, as NN inputs and the partitioning of the total energy into atomic contributions ensure that all quantities computed with the NN (energies, analytical forces, and stress tensors) are invariant with respect to rigid translations and rotations of the whole system and to atoms exchanges. Once the fit is obtained, the NN potential can be applied to systems containing an arbitrary number of atoms. Details of the high-dimensional NN method are given elsewhere [4,7].

To generate our NN potential for the bulk phases of GeTe, we fitted the density-functional total energy of about 30000 configurations of 64-, 96- and 216-atom supercells. In total, about two billions of local atomic environment were taken into account. We started with a relatively small dataset of about 5000 structures, which include crystalline configurations, snapshots of the liquid phase and of the amorphous phase generated by quenching from the melt at normal conditions and at high pressure. We also considered mixed crystalline/amorphous models generated by partially crystallizing the amorphous phase in ab-initio molecular dynamics simulations at high temperature. This first dataset was then expanded adding random or locally distorted structures, slight deviations in stoichiometry and snapshots of high temperature MD simulations of the liquid phase at different densities. All these configurations were generated by ab-initio molecular dynamics simulations with the code CP2k within the computational framework discussed in our previous works [2]. The accuracy of the reference ab initio energies is of paramount importance while training the NN. Ab initio energies for each configuration in the dataset were then calculated using the QUANTUM-ESPRESSO package [8] at full convergence in Brillouin Zone (BZ) integration. Perdew-Burke-Ernzerhof (PBE) [9] exchange-correlation functional and norm conserving pseudopotentials were employed, considering only the outermost s and p electrons in the valence. Kohn-Sham (KS) orbitals were expanded in a plane waves basis up to a kinetic cutoff of 40 Ryd and BZ integration was performed over a 4x4x4 Monkhorst-Pack mesh [10]. These settings ensure convergence of the total energy within 2 meV/atom. The local environment of each atom is defined by the value of 159 symmetry functions (see [7] for details) defined in terms of the positions of all neighbors within a distance cutoff of 6.879 Å. The generation of the NN potential and the NN molecular dynamics simulations are performed with the code RuNNer [11]. Although the generation of the NN potential is computationally very demanding due to the very many ab-initio reference calculations, systems as large 4000 atoms can then be easily studied with a computational load five order of magnitude lower than that of an equivalent density functional calculation. The simulation of 4000-atom cells takes 1.5 min/ps on a 256 cores of a Cray XT5 computer.

3. RESULTS & DISCUSSION

Results from NN and ab-initio calculations are here compared for the crystalline, liquid and amorphous phases.

Crystalline phase. The theoretical structural parameters of the trigonal phase of GeTe at equilibrium are a=4.45 Å, α=55.5° and u=0.035 to be compared with the experimental value of a=4.31 Å, α=57.9 and u=0.026. The difference in energy between the trigonal phase and a fictitious perfect cubic phase at its equilibrium density is 55 eV/atom and 44 eV/atom in ab-initio (at full convergence in BZ integration) and NN calculations.
The phonon density of states at zero temperature computed ab-initio [3] and with the NN potential (mesh in q space 5x5x5) are compared in Fig. 1a. The agreement is satisfactory considering than long range interactions are not present in the NN potential.
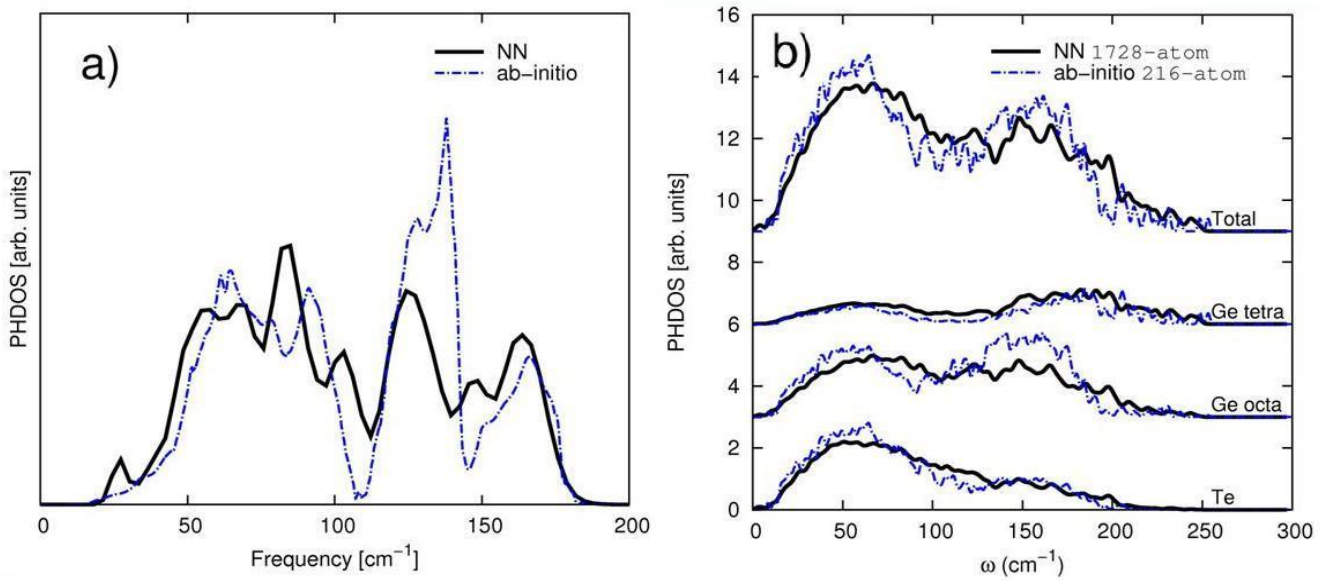

Figure 1. a) Phonon density of states of crystalline GeTe at zero temperature computed ab-initio (dashed line, Ref. [3]) and with NN potential (continuous line). b) Phonon density of states of amorphous GeTe from a 1728-atom NN model and a 216-atom ab-initio model. Only phonons at the supercell Γ-point are considered. The higher smoothness of NN data is due to the larger supercell used. Projections of the DOS on Ge and Te atoms are also shown.

Liquid. The liquid was simulated by a 4096-atom cubic supercell at 1150 K. The partial pair correlation functions are compared with ab-initio data from a simulation at the same temperature with a 216-atom cell. The computational details of the ab-initio simulations are the same as those reported in Ref. [3]. The self-diffusion coefficient of the two species from the NN simulation are D_{Ge}= 4.96 10^{-5} cm^2/s and D_{Te}= 3.62 10^{-5} cm^2/s to be compared with the ab-initio values of D_{Ge}= 4.65 10^{-5} cm^2/s and D_{Te}= 3.93 10^{-5} cm^2/s at the same temperature.

Amorphous. The amorphous phase was generated by quenching the molten sample from 1150 K to 300 K in 100 ps. The partial pair correlation functions of the amorphous are compared in Fig. 2 with ab-initio data of a 216-atom cell [3]. Doubling the quenching time does not introduce sizable differences in the partial pair correlation functions reported in Fig. 2. Also decreasing the system size from 4096-atom to 1728-atom produces essentially the same

results on the scale of Fig.2. Coordination numbers are assigned by integrating the pair correlation functions up to a cutoff distance of 3.2 Å for all species which corresponds to the outer edge of the Ge–Te pair correlation function. The angle distribution function and the distribution of coordination numbers for Ge and Te in the amorphous phase from NN and ab-initio simulations are compared in Fig. 3.

The phonon density of states (DOS) of the amorphous phase from NN and ab-initio simulations are compared in Fig.1b. Phonon frequencies are computed by diagonalizing the dynamical matrix obtained in turn from the variation of atomic forces due to finite atomic displacements 0.0053 Å large. Only phonons with the periodicity of the supercell (Γ-point phonons) are considered. Ab-initio phonons are computed in a 216-atom cell while NN phonons are obtained from the 1728-atom cell.
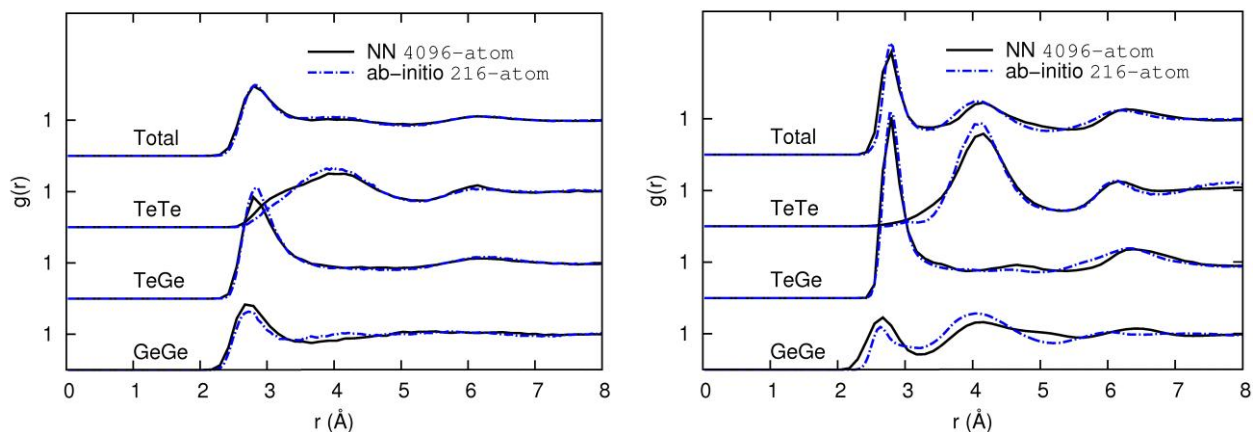

Figure 2. Left panel: partial pair correlation functions of liquid GeTe from a NN simulation at 1150 K with a 4096-atom cell (continuous line) compared with results from an ab-initio simulation at the same temperature and a 216-atom cell (dashed lines). Right panel: partial pair correlation functions of amorphous GeTe from a NN simulation at 300 K with a 4096-atom cell (continuous line) compared with results from an ab-initio simulation at the same temperature and a 216-atom cell (dashed lines).
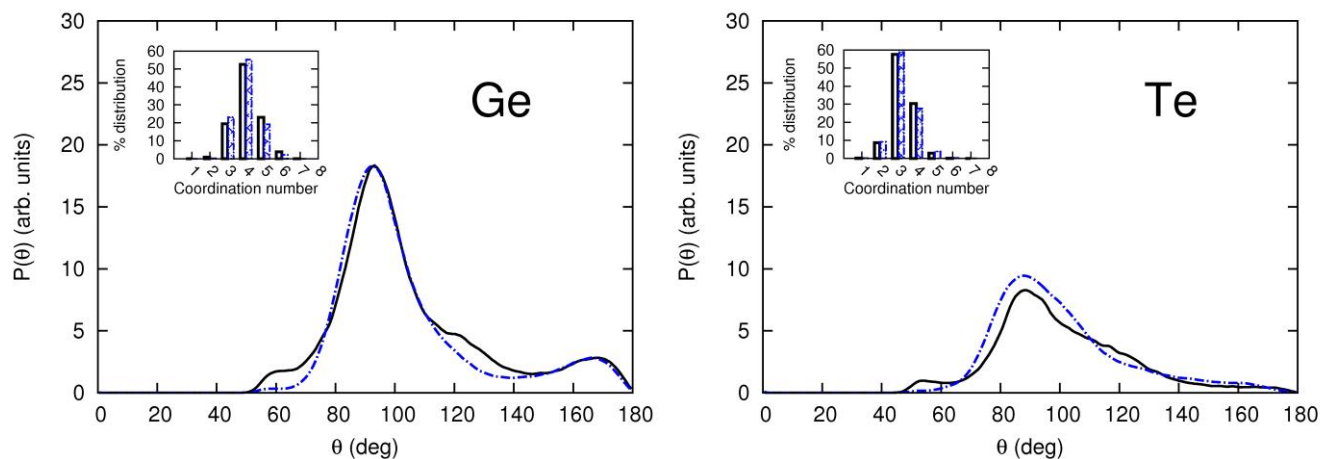

Figure 3. Angle distribution function and distribution of coordination numbers (inset) of the amorphous 4096-atom model generated with the NN potential (continuous lines) compared with ab-initio data from a 216-atom cell (dashed lines).

4. CONCLUSION

In summary, a NN potential for GeTe was generated and tested to reproduce properties of the different phases. The NN potential was validated by comparing structural and dynamical properties of the crystalline, liquid and amorphous phases with satisfactorily results. The development of classical potentials with close to ab-initio accuracy   represents a breakthrough in the simulation of phase change materials. It will allow one to address several key issues on the properties of materials in this class that are presently beyond the reach of ab-initio simulations. Applications to the study of the crystalline/amorphous interface, of the thermal conductivity in the amorphous phase and of the homogeneous and heterogeneous crystallization of the amorphous are in progress.

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Biographies

Marco Bernasconi received the undergraduate degree in Physics at the University of Milano in 1988 and the Phd in Theoretical Condensed Matter Physics at Sissa (Trieste) in 1993. He spent two years as a postdoc at the Max-Planck-Institut fuer Festkoerperforschung (Stuttgart, Germany) in the group of Prof. M. Parrinello and then joined the Department of Materials Science of the University of Milano-Bicocca (Milano, Italy) where he currently holds the position of associate professor in Condensed Matter Physics. His research activity has been devoted to the ab-initio modelling of materials ranging from amorphous semiconductors and insulators for applications in microelectronic and photonics to fast ion conductors and low-Z superconductors. He is author of 104 articles in international journals with peer review among which 11 deal with the properties of phase change materials.