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Sensitivity to Dispersion Forces in First-Principles Modeling of Disordered Chalcogenides

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The inclusion of dispersion (van der Waals, vdW) forces in first-principles modeling of disordered chalcogenides is analyzed and critically discussed in view of their impact on the atomic structure. To this purpose we considered the case of glassy $GeTe_4$. We selected a vdW correction (termed vdW_G hereafter) introduced by Grimme (2006) and, as an alternative, the approach (termed vdW_W hereafter) based on the Wannier functions formalism (Silvestrelli, 2008). It appears that a strategy based on the update of the vdW interactions due to changes in the electronic structure during the dynamical evolution (i.e., the vdW_W one) provides results clearly different from those obtained in the vdW_G framework. By keeping in mind that the nature of the present results is preliminary and reflect a trend to be confirmed, we draw attention to the different levels of agreement with experimental data obtained with the two vdW schemes employed.

Keywords: Car-Parrinello molecular dynamics (CPMD), atomic structure, di-chalcogenides, van der Waals, amorphous materials

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1. INTRODUCTION

Chalcogenide glasses have a tremendous range of potential applications, as they can be found in sensitive media for optical recording, re-writable discs, nonvolatile memory devices, and optical materials (lasers, fiber optics, and optical lenses for infrared transmission) (Boolchand and Bresser, 2001; Huang et al., 2004; Kato et al., 2006; Le Roux et al., 2012). Their non-trivial atomic structure has long been a challenge for measurements, stimulating the application of realistic theoretical approaches at the density functional theory (DFT) level. Quite recently, several contributions in this area have been devoted to the impact of dispersion forces on first-principles molecular dynamics (FPMD) descriptions of disordered chalcogenide materials (Micoulaut, 2013; Micoulaut et al., 2014, 2017; Bouzid et al., 2015b; Lampin et al., 2017). We recall that dispersion forces are not included in the original Kohn-Sham DFT formalism, calling for the addition of appropriate corrections bound not to alter the first-principle character of the model description. In the case of disordered network-forming chalcogenides, dispersion forces are more likely to play a role in Ge_xTe_{1-x} than in Ge_xSe_{1-x} systems. This is exemplified, for instance, by the behavior of glassy $GeTe_4$ (g-$GeTe_4$), proved to be much more sensitive to dispersion forces (Micoulaut, 2013; Bouzid et al., 2015b) than g-$GeSe_4$ or g-GeS_4 (Chaker et al., 2018b). Compelling evidence on the impact of vdW forces for Te-rich ternary glasses has been also collected for $Ga_{10}Ge_{15}Te_{75}$ (Chaker et al., 2018a). The above results have been obtained by exploiting the vdW scheme due to Grimme (vdW_G), in particular in the version named D2 (Grimme, 2006). This approach has an extended record of reliability, resulting from its capability to account properly for the action of dispersion forces in a large variety of systems. As such, at a first sight, one might tend to conclude that unambiguous information exists on how the atomic structure of disordered chalcogenides is affected by the inclusion of dispersion forces.

However, a word of caution is in order to put these findings in the right perspective. Indeed, the Grimme formalism is not built on any update of the vdW interactions due to changes in the electronic structure occurring during the dynamical evolution. This is somewhat awkward in light of the strong interplay between electronic structure and ionic positions inherent in FPMD. A revealing example was provided by the case of liquid $GeSe_2$, for which an alternative description was employed for the dispersion forces, the vdW_W one (Lampin et al., 2017). In this case the electronic structure, obtained within the selected DFT-GGA (generalized gradient approximation) framework, is used to compute the maximally localized Wannier functions (MLWF) on which the van der Waals scheme is based.[1] Considering liquid $GeSe_2$, we found that the MLWF approach reproduces existing first-principles atomic structures while the vdW_G one is less performing in the case of the Ge-Ge pair correlation function (Lampin et al., 2017). Turning to glassy $GeSe_4$ and glassy GeS_4, the two vdW approaches were found to agree to a large extent, exceptions again occurring for some moderate differences in the intensity of the peaks in the Ge-Ge pair correlation function (Chaker et al., 2018b).

These results drive two considerations. First, the impact of dispersion forces on disordered chalcogenides might differ when adopting different theoretical schemes. This is more unexpected than any dependence on dispersion forces resulting from a mere change in the chemical composition within a given family of compounds. Second, more importantly, the inclusion of such an additional *ad hoc* part in the Kohn-Sham Hamiltonian can lead to quite different effects when the scheme (the vdW_W one) evolves in time with the electronic structure. In view of their higher sensitivity to dispersion forces, it is desirable to consider the case of Te-rich disordered chalcogenides. Glassy $GeTe_4$ is well suited to this purpose due to the availability of results obtained within the vdW_G approach. We fulfill this goal with the present study, in which we produce new vdW_W data on the structural properties of glassy $GeTe_4$ and we compare them with experiments and the vdW_G counterpart available in Bouzid et al. (2015b).

This study shows that the impact of dispersion forces on glassy $GeTe_4$ turns out to be dependent on the recipe employed to model the vdW correction (vdW_G *vs* vdW_W schemes). When compared to the case of Ge_xSe_{1-x} chalcogenides, this is indicative of an effect that is stronger when the sensitivity to the inclusion of dispersion forces is higher. The notion of structural properties dependent (even moderately) on the methodology employed to model dispersion forces has to be handled with great care, since it can deeply affect the precise assessment of the atomic structures and bonding properties of glasses.

This paper is organized as follows. In section 2, we provide the methods and computational details of the calculations performed in this work with a special emphasis on the scheme employed to account for the vdW interactions in glassy $GeTe_4$. In section 3, we focus on the total and partial pair correlations functions to show the impact of the different dispersion schemes on the structural properties. In section 4, we underline the novelty, importance and consequences of our findings in the framework of first-principle calculations of disordered systems accounting for vdW corrections.

2. COMPUTATIONAL METHODS

Our simulations of glassy $GeTe_4$ were performed within the Car-Parrinello (Car and Parrinello, 1985) molecular dynamics (CPMD) scheme as implemented in the CPMD code (Hutter et al., 1995). We employ the exchange functional proposed by Becke (1988) and the correlation functional due to Lee et al. (1988) (BLYP). For the treatment of the core-valence interactions, we adopted a norm-conserving pseudo-potential according to the description of Troullier and Martins (1991). A plane wave basis set is chosen for the representation of the valence electrons with a corresponding energy cutoff of 40 Ry (Bouzid et al., 2015a,b; Lampin et al., 2017). The Brillouin zone integration is restricted to the Γ point.

Keeping in mind that the DFT-D2 formula proposed by Grimme (2006) was employed in a recent investigation (Bouzid et al., 2015b), we turn to an alternative recipe (vdW_W) for comparative purposes. It is appropriate in this context to recall the main foundations of this scheme, by referring the reader for details to the original papers thoroughly illustrating this formalism and the connections with the concept of maximally localized Wannier functions (MLWFs) (Wannier, 1937; Silvestrelli et al., 1998; Ikeda and Boero, 2015). Accordingly, one writes the vdW interaction in the standard way (Andersson et al., 1996), namely:

$$E_{vdW} = -\sum_{n<l} f(r_{nl}) \frac{C_{6,nl}}{r_{nl}^6}, \tag{1}$$

where the subscripts n and l run over all atoms or fragments into which the system is partitioned and $f(r_{nl})$ is a damping function avoiding double counting of correlations at short range. The $C_{6,nl}$ coefficients can be expressed in terms of the local electronic density $\rho_n(\mathbf{r})$ as

$$C_{6,nl} = \frac{3}{32\pi^{3/2}} \int_{r \le r_{\rm cut}} \int_{r' \le r_{\rm cut}} \frac{\sqrt{\rho_n(\mathbf{r})} \cdot \sqrt{\rho_l(\mathbf{r}')}}{\sqrt{\rho_n(\mathbf{r})} + \sqrt{\rho_l(\mathbf{r}')}} d^3r' d^3r. \tag{2}$$

Within DFT, the applicability of this relationship is not straightforward since the total electronic density $\rho(\mathbf{r})$ cannot be

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[1] More details on the MLWF formalism are given later in the section devoted to the methodology.

rigorously defined locally. To overcome this difficulty, we resort to the MLWFs $w_n(\mathbf{r})$ by rewriting the former definition as

$$C_{6,nl} = \frac{3}{32\pi^{3/2}} \int_{r\le r_{\rm cut}} \int_{r'\le r_{\rm cut}} \frac{w_n(\mathbf{r})\cdot w_l(\mathbf{r}')}{w_n(\mathbf{r})+w_l(\mathbf{r}')}\, d^3r'\, d^3r. \qquad (3)$$

In this case, r_{nl} is the distance between two MLWF centers on pairs of fragments into which the system is partitioned. MLWFs can be calculated *on the fly* during the CPMD run. In the x-direction (with L the supercell size) the MLWF centers are defined as

$$x_n = -\frac{L}{2\pi}\Im m\left\{\log\left(\langle w_n|\exp(-2i\pi\cdot x/L)|w_n\rangle\right)\right\}, \qquad (4)$$

with analogous expressions holding for the y and z directions.

During our first-principles molecular dynamics runs of glassy $GeTe_4$ in the vdW_W framework, the temperatures of the ions and of the fictitious electronic degrees of freedom were controlled via Nosé-Hoover thermostats (Nosé, 1984; Hoover, 1985; Blöchl and Parrinello, 1992). An integration step of 5 au (0.168 fs) ensured an optimal control of the conserved quantities all along the molecular dynamics trajectories.

As in Bouzid et al. (2015b) our system is made of 215 atoms (43 Ge, 172 Te) in a cubic supercell of edge equal to 19.24 Å. By taking as initial set of positions one configuration extracted from the trajectory produced in Bouzid et al. (2015b), a temporal cycle was implemented to lose memory of this starting condition. The initial system was brought at an ionic temperature of T = 900 K in 88 ps and equilibrated at that temperature during about 50 ps. Then, the temperature was lowered to T = 300 K for 35 ps to conclude with an additional run of 30 ps exploited for the structural analysis.

In what follows, we concentrate on the total pair correlation function $g_T(r)$ obtained as a weighted linear combination of the three partial pair correlation functions $g_{\alpha\beta}(r)$, where α and β denote the chemical species considered (Ge, Te). Without resorting to an exhaustive report of structural properties, our purpose is to highlight a few, striking observations of the behaviors recorded in the absence (NovdW data hereafter) and in the presence of dispersion forces, these latter expressed in two different forms (vdW_W, present results, vdW_G Bouzid et al., 2015b).

3. RESULTS: TOTAL AND PARTIAL PAIR CORRELATION FUNCTION

The results presented in Bouzid et al. (2015b) showed that the best comparison with the available experimental data for g-$GeTe_4$ is the one obtained through the BLYP exchange-correlation functional when used in conjunction with the vdW forces. In particular, the total pair correlation function was closer to experiments than when using the scheme due to Perdew, Burke and Ernzerhof (PBE) (Perdew et al., 1996, 1997). The resulting network is made by a dominant tetrahedral arrangement with a small number of coordination defects. In that paper, two kinds of conclusions were drawn. First, the results confirmed the importance of accounting for vdW dispersion forces when modeling Ge-Te chemical bonding in disordered binary chalcogenides. Second (more important since not dependent on the specific dispersion correction employed) we noticed that the account of vdW forces is less crucial that a change in the exchange-correlation functional (from PBE to BLYP in this specific case). The results contained in **Figure 1** challenge the first set of conclusions referred to above. Four sets of data are reported, namely experiments (Kaban et al., 2003) and simulations without (NovdW) and with [vdW_G (Bouzid et al., 2015b), vdW_W (present work)] dispersion forces. It appears that the vdW_W approach lies very close to the NovdW data, thereby underlying an artificial effect inherent in the use of the vdW_G recipe.

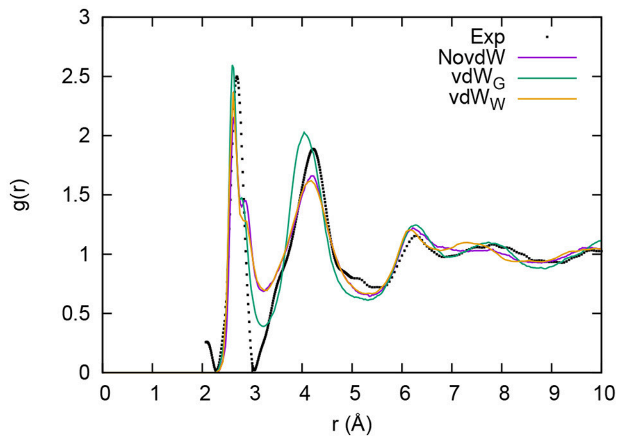

FIGURE 1 | Total correlation function of g-$GeTe_4$. Results with no inclusion of vdW interactions (purple line) and with inclusion of vdW interactions following the Grimme scheme (vdW_G, green line) (as reported by Bouzid et al., 2015b) are compared to those including van der Waals interaction in the vdW_W formalism (orange line). Experiments are from Kaban et al. (2003).

To corroborate the above findings in terms of atomic arrangements between the different pairs of atoms, we resort to the partial pair correlation functions. These results are reported in **Figure 2**.

For the Ge-Te pair correlation functions, the results obtained by the three methods are essentially identical, to indicate that the shortest range interactions are not affected by the inclusion of a dispersion scheme. In the Ge-Ge case, the intensities of the first peaks are unequal, indicating small changes in the number of homopolar Ge-Ge bonds. However, vdW_G yields by far the most intense first peak. More striking is the difference recorded in the region around $r \simeq 4$ Å , where the second peak is definitely much higher in the vdW_G case, vdW_W, and NovdW data being quite close. The consequences of the use of vdW_G in comparison with the vdW_W and NovdW cases are clearly noticeable in the g_{TeTe} pair correlation function. The pronounced first minima exhibited by g_{TeTe} in the Grimme framework disappear when considering instead the MLWF-based scheme vdW_W. Altogether, in the Te-Te case, the effect is quite striking since the profiles of the NovdW and vdW_W Te-Te correlation functions are essentially superposed.

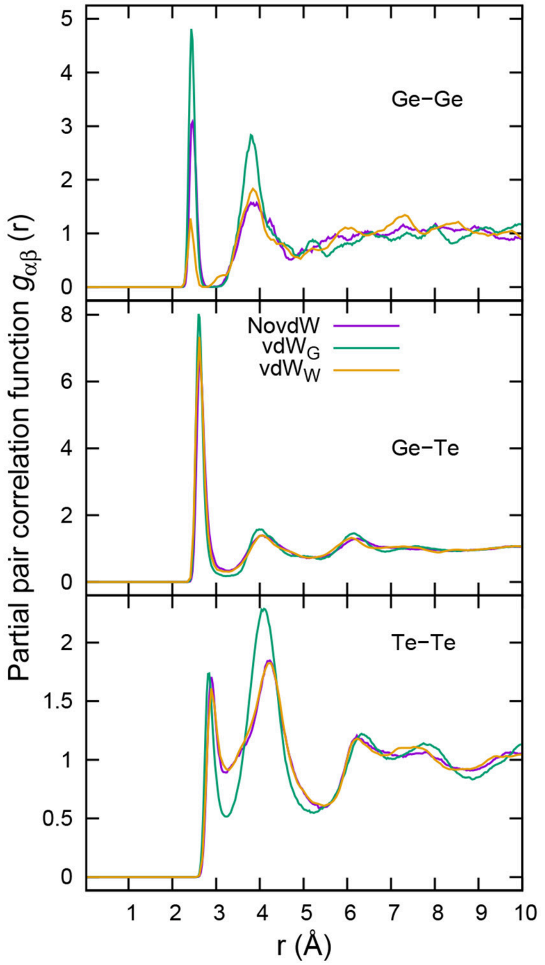

FIGURE 2 | Partial pair correlation functions of *g*-$\mathrm{GeTe_4}$. Results with no inclusion of vdW interactions (purple line) and with inclusion of vdW interactions following the Grimme scheme ($\mathrm{vdW_G}$, green line) (as reported by Bouzid et al., 2015b) are compared to those including van der Waals interaction in the $\mathrm{vdW_W}$ formalism (orange line).

4. DISCUSSION AND CONCLUSIONS

There is a widespread interest in a precise understanding of the impact of dispersion forces on the structural properties of certain classes of disordered materials, such as chalcogenide glasses. When considering networks predominantly based on Te, some pieces of evidence have been produced to prove that such impact cannot be excluded, models containing dispersion forces appearing somewhat closer to experimental counterparts (Micoulaut et al., 2014, 2017; Bouzid et al., 2015b). The present work intends to alert the modeling community on the sensitivity of glassy structural data to different schemes for the dispersion forces. In particular, we show explicitly what happens when one uses a recipe better accounting for the relationship between the van der Waals coefficients and the electronic structure. To this purpose we have produced three models, characterized by the absence of dispersion forces and by the account of dispersion forces in the Grimme scheme ($\mathrm{vdW_G}$) (Grimme, 2006) or in the Maximally Localized Wannier scheme ($\mathrm{vdW_W}$) (Silvestrelli, 2008). In this approach the van der Waals coefficients adapt to changes undergone by the electronic structure during the motion. We found that the $\mathrm{vdW_W}$ strategy produces structural data in very good agreement with those obtained in the absence of any account of dispersion forces, thereby differing from the findings previously obtained by adopting $\mathrm{vdW_G}$. However, and quite puzzlingly, $\mathrm{vdW_G}$ features a better agreement with experimental data (pair correlation functions). As a contribution to the debate on the performance of the different van der Waals approaches, it is worth recalling that the general applicability of the Grimme formalism was questioned in the case of glassy GeTe (Raty et al., 2015). This has motivated the use of an alternative scheme proposed by Lee et al. (2010). Conceptual issues related to the proper inclusion of dispersion forces within density functional theory have been extensively reviewed and analyzed in Klimeš and Michaelides (2012).

In view of the consequences implied by our findings, we do find appropriate to stress the preliminary character of the present results, since they need to be confirmed by a full assessment of their statistical accuracy (i.e., through the production of several equilibrium trajectories) and by the use of alternative schemes for the dispersion forces [as the ones given in (Lee et al., 2010) and in (Tkatchenko and Scheffler, 2009)]. However, the mere observation of what we found with one trajectory is already quite compelling in terms of similarities between the total and partial correlation functions for the NovdW and the $\mathrm{vdW_W}$ cases. The question arises on the capability of dispersion forces recipes to play a role when they cannot be considered negligible and, in turn, vanish when their specific weight is much smaller in comparison to other bonding contributions. Our results indicate that this cannot be always the case, thereby rising an unexpected ambiguity on the actual consistency of such schemes. Should these findings be confirmed, it would be desirable to reconsider any known statement on the expected impact of dispersion forces in the case of disordered chalcogenides, with particular attention devoted to Te-based ones.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication .

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