Computational Materials Science 152 (2018) 146–150

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Van der Waals interactions and the properties of graphite and 2H-, 3R- and 1T-MoS_2: A comparative study

Florence P. Novais Antunes[a,*], Viviane S. Vaiss[a], Sérgio R. Tavares[a], Rodrigo B. Capaz[b], Alexandre A. Leitão[a]

[a] Departamento de Química, Universidade Federal de Juiz de Fora, Juiz de Fora, MG 36036-330, Brazil
[b] Instituto de Física, Universidade Federal do Rio de Janeiro, Caixa Postal 68528, Rio de Janeiro, RJ 21941-972, Brazil

ARTICLE INFO

Keywords:
DFT calculations
Molibdenum disulfide
Graphite
Elastic properties
Structural properties

ABSTRACT

We performed *ab initio* calculations based on density functional theory (DFT) in order to explore the influence of van der Waals (vdW) interactions on the structural, energetic, elastic and vibrational properties of graphite and MoS_2 (in the 2H, 1T and 3R polytypes). Different vdW functionals were tested and their performance were evaluated by the comparison with the available experimental data for graphite and 2H-MoS_2. Several properties of the 1T- and 3R-MoS_2 phases were also predicted.

1. Introduction

Two-dimensional (2D) materials drew great attention in the past few years as possible new materials for electronics, among other applications. Up to now, the most studied 2D materials are graphene [1] and semiconducting transition metal dichalcogenides (TMDs), such as MoS_2 [2]. These materials and their heterostructures offer excellent mechanical flexibility, optical transparency, and favorable transport properties for developing electronic, sensing, and optical devices [3]. The intrinsic semiconducting nature of MoS_2 is a major advantage over graphene (which has no intrinsic band gap) as a two-dimensional (2D) channel material in field-effect transistors (FET). Also, being a direct gap material, 2D MoS_2 has great potential for application as optical material as well.

Despite the recent interest in their 2D forms, both systems are also extremely well-known in their traditional 3D, bulk form, i.e. graphite and molybdenite, and they share a few common properties [4]. They both have hexagonal and layered structures, in which the covalent-bonded layers are held together by weak van der Waals forces. Due to its high temperature stability, chemical inertness, high thermal conductivity, low thermal expansion and high ion-exchange capabilities, graphite is widely used in many industrial applications [5]. Also, molybdenite and other TMDs are extensively used in catalysis, energy storage, hydrogen generation, dehydrosulfurization and lubrication [6].

During the synthesis of MoS_2, both hexagonal (2H) and rhombohedral (3R) polytype layered crystals, which present somewhat different physical properties, can be obtained. For example, the 3R polytype of MoS_2, due to its non-centrosymmetric structure, exhibits a valley polarization in photoluminescence emission even in the bulk form. The electronic properties of 3R phase remain largely unexplored and it is not possible to distinguish the polytype *in situ* experimentally. The 1T phase is produced by the oxidation of $KMoS_2$ or $LiMoS_2$ and is metastable, being easily converted to the disordered 2H phase after heating in the temperature of 100 °C [8–10]. Due to the complex nature of the layered TMD materials and the great interest in the electronics community for their applications in emerging devices, a more reliable, accurate, and atomistic treatment of the structural and electronic properties of TMD is desired [7].

Density functional theory (DFT) is the tool of choice for the structural investigation of various types of materials [11,12]. Although the chemical bonding between nearest neighbors determines the structure in small molecular systems, for molecular assemblies and for systems of greater sizes, the weak intermolecular forces start to play a more determining role in their stabilization. To cope with this challenge, a good level of theory should have at its disposal the appropriate total energy functionals which take into account the correct weak intermolecular interactions. However, popular density functionals such as the ones based on generalized gradient approximations (GGAs) are unable to describe the correct van der Waals interactions resulting from dynamical correlations between fluctuating charge distributions, therefore they are intrinsically unadapted to describe structural and energetic properties of molecular materials. Several routes have been proposed to circumvent this difficulty. One route is through the so-called "dispersion-corrected" (DFT-D) functionals [13], which consist of a pragmatic

---

[*] Corresponding author.
E-mail addresses: florence.novais@ice.ufjf.br (F.P. Novais Antunes), alexandre.leitao@ufjf.edu.br (A.A. Leitão).

https://doi.org/10.1016/j.commatsci.2018.05.045
Received 4 September 2017; Received in revised form 3 May 2018; Accepted 21 May 2018

and inexpensive addition of a semiempirical dispersion potential to the conventional Kohn-Sham DFT energy. In this method, the van der Waals interactions are described via a simple pairwise force field optimized for popular DFT functionals, such as PBE, PW91 and B3LYP. Among numerous attempts to provide consistent parametrizations compatible with a given exchange-correlation functional, the DFT-D2 approach of Grimme seems to be one of the most successful ones [14]. It is noteworthy that a more recent Grimme-like approach exists, namely DFT-D3, although it has not been yet implemented in Quantum Espresso.

Another route is through the van der Waals density functionals (vdW-DF) [15], which are built by adding a non-local contribution to the electronic energy density-functional so as to describe dispersion interactions between electronic densities at arbitrary geometries. We employed vdW-DF1 [16], vdW-DF2-B86R, vdW-DF2-C09 [17,18] and vdW-DF-CX [19] implementations in this work [20].

In this work, after extensive testing of several approaches for the treatment of dispersion interactions for the well-studied graphite, 1T- and 2H-MoS_2 systems, we calculated and predicted properties of the 3R-MoS_2 and 1T-MoS_2 polytypes, for which there is little information available in the literature [23]. Our results indicate that the vdW-DF2 framework functionals have the best overall performance among the studied functionals for this class of systems.

2. Methodology

Ab initio calculations were performed in the framework of DFT using the Quantum Espresso package [21]. We used a variety of functionals for the exchange-correlation such as LDA [22], PW91 [24], PBE [25], revPBE [26], PBESOL [27]. The use of a large collection of XC functionals is important for the evaluation of different flavors of the GGA approximation. We used Vanderbilt ultrasoft pseudopotentials to describe the ion cores [28]. The Kohn-Sham orbitals were expanded in a plane wave basis set with a maximum kinetic energy of 60 Ry. Monkhorst-Pack [29] meshes of $6 \times 6 \times 2$ k-point sampling in the first Brillouin Zone were used for the MoS_2 bulk in the polytypes 2H and 3R, $7 \times 7 \times 5$ for the graphite bulk and $3 \times 3 \times 3$ for the 1T polytype.

Dispersion interactions were included via the DFT-D2 [14], vdW-DF1 [16], vdW-DF-B86R, vdW-DF2-C09 [17,18] and vdW-DF-CX [19] approaches. In the case of DFT-D2, a semiempirical pairwise interatomic potential is added to the DFT converged total energy. This additional term results from the computation of the dispersion energy taking into account the periodic boundary conditions by the means of a real-space summation. Formally, the resulting total energy is then given by:

$$E_{DFT-D2} = E_{DFT} + E_{disp} \tag{1}$$

where E_{DFT} is the converged total energy with the chosen functional and E_{disp} is the contribution of the dispersion interactions computed within an interatomic pairwise approach. The term E_{disp} can be written as:

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}) \tag{2}$$

where N_{at} is the total number of atoms, C_6^{ij} denotes the dispersion coefficient between the atomic sites i and j, R_{ij} is the distance between atoms i and j, s_6 is a semiempirical parameter corresponding to an overall scaling of dispersion interactions and, to avoid singularities between very close neighbors when R_{ij} is very small, a damping function f_{dmp} is used. In the present work, the s_6 parameter was fitted for PBE and PW91 with the experimental values of the parameter c. Therefore, the predicted properties from this approach were all computed by these fitted parameters. For graphite, the optimal values are 0.45 and 0.50 for PW91-D2 and PBE-D2, respectively. In the case of the 2H-, 3R- and 1T-MoS2, the optimized values are 0.95 for both PBE-D2 and PW91-D2 for 3R- and 1T-, 0.90 for PW91-D2 and 0.95 for PBE-D2 for 2H For the sake of simplicity, "-D2" will be appended to the name of the exchange-correlation functional in order to state that the DFT-D2 approach was applied.

In the case of the vdW-DF1, vdW-DF2-B86R, vdW-DF2-C09 and vdW-DF-CX approaches, dispersion interactions are computed self-consistently from the electronic density. The exchange-correlation functional framework is written as:

$$E_{xc}[n] = E_x^{GGA} + E_c^{LDA} + E_c^{nl}, \tag{3}$$

where E_c^{LDA} is the local-density approximation correlation functional, E_x^{GGA} is the semilocal exchange energy and E_c^{nl} is the non-local dispersion, generally written as

$$E_c^{nl}[n] = \frac{1}{2} \iint d^3 r_1 d_2^3 n(\vec{r_1}) n(\vec{r_2}) \phi(q_1, q_2, r_{12}), \tag{4}$$

where $r_{12} = |\vec{r_1} - \vec{r_2}|$, q_i is the inverse length scales at positions $\vec{r_i}$ and ϕ is the dispersion kernel.

All structures were found by minimizing the total energy and the atomic forces with the convergence criteria of 10^{-4} Ry and 10^{-3} Ry/Bohr, respectively.

The exfoliation energies of systems were determined by the following equation

$$E_{exf} = E_{monolayer} - E_{bulk} \tag{5}$$

where $E_{monolayer}$ and E_{bulk} are the total energies of the monolayer and the bulk systems, respectively. The bulk energy was normalized by the number of the layers per unit cell. Cohesive energies were calculated as

$$E_{coh} = \sum_i E_i - E_{bulk} \tag{6}$$

where E_{bulk} and E_i are the total energies of the bulk and of a single atom i in vacuum.

Bulk moduli were calculated by fitting $E(V)$ curves to the Murnaghan's equation of state:

$$E(V) = E_0 + V\left(\frac{B}{B'}\right)\left[\left(\frac{V_0}{V}\right)^{\frac{B'}{B'-1}} + 1\right] - \frac{BV_0}{(B'-1)} \tag{7}$$

where E_0 is the minimum energy, V_0 is the equilibrium volume, B is the bulk modulus, and $B' = \frac{dB}{dP}$ is the pressure derivative of the bulk modulus.

Of particular interest in the evaluation of vdW functionals is the calculation of the elastic constant C_{33}

$$C_{33} = \frac{2c_0}{\sqrt{3}\, a_0^2} \frac{\partial^2 E}{\partial c^2}, \tag{8}$$

since it involves the relative displacements between vdW-interacting rigid layers. In the equation above, a_0 and c_0 are in-plane and out-of-plane lattice constants at equilibrium. Closely related to C_{33} is the frequency ω_{LB} (in cm^{-1}) of the interlayer-breathing (or ZO′) phonon mode: $\omega_{LB} = \sqrt{\frac{C_{33}}{\mu \pi^2 v^2 t}}$ [30], where μ is the area mass density for the monolayer, v is the light speed (in cm/s) and t is the interlayer distance.

3. Results and discussion

3.1. Structural analysis

Table 1 presents the main unit cell parameters obtained by the different approaches. The largest deviations with respect to the experimental values occur for the c parameter, certainly because of the poor treatment of the dispersion interactions for some functionals. For graphite, LDA and vdW-DF2 framework present the lowest relative errors, whereas the values obtained with PBE, PW91 and revPBE present the highest deviations from the experimental values. Regarding the dispersion corrections, the DFT-D2 approach tends to overbind the graphite layers. It should be noted that the good structural description