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# Reparameterization of REBO-CHO for graphene-oxide molecular dynamics simulations

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The Reactive empirical bond order (REBO) potential developed by Brenner *et al.*<sup>1,2</sup> for molecular dynamics (MD) simulations of hydrocarbons, and recently extended to include interactions with oxygen atoms by Ni *et al.*<sup>3</sup> is modified for graphene-oxide (GO). Based on DFT calculations, we optimized the REBO-CHO potential to improve its ability to calculate the binding energy of an oxygen atom to graphene and the equilibrium C-O bond distances. In this work, the approach towards the optimization is based on modifying the bond order term. The modified REBO-CHO potential is applied to investigate the properties of some GO samples.

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## I. INTRODUCTION

Classical molecular dynamics (MD) methods are powerful tools for atomistic simulations of many physical properties of diverse material systems composed from thousands to billions of atoms, especially when quantum mechanics simulations are prohibited by computational limitations. Consisting of a numerical integration of the Newton's equations, classical MD methods use empirical potentials to approximate the interaction between atoms. The challenge of empirical potential development is to obtain an accurate interatomic potential energy function of the system which not only captures most of physical and chemical properties of the atoms that compose the system and their interactions, but also generates good predictions of the physical properties of all system environments.

Adjacent elements of the periodic table may present very different chemical and physical properties, which makes it difficult to establish a single universal classical potential to handle all the elements. The consequence is that many different potentials have been developed for different classes of elements and for different purposes. For example, the first and second generation reactive bond order potential (REBO)<sup>1,2</sup>, which together with the adaptive intermolecular reactive bond order potential (AIREBO)<sup>4</sup> are optimized for hydrocarbon materials, the embedded atom method (EAM)<sup>5</sup> and modified EAM (MEAM)<sup>6</sup> which is optimized for metals and alloys but includes some parameterizations for metal oxides, and the chemistry at Harvard macromolecular mechanics (CHARMM) force field<sup>7</sup> which is targeted towards biomolecules, and many others not cited. However, recently potentials have been developed that can be used for a variety of material systems regardless of bonding type. For example, the charge-optimized many body (COMB) potential is suitable for a variety of metals, covalent semiconductors, and their oxides<sup>8-11</sup>, and the reactive force field (ReaxFF)<sup>12</sup> has been parameterized for a large variety of systems, including covalently bound, metallic, and ionic materials.

Our interest lies in the second generation REBO and AIREBO potentials, where the latter consists of an additional torsional term and a switching function to van der Waals interactions. They are largely used to study the physical and chemical properties of carbon structures<sup>13-19</sup>. Recent examples of successful studies performed with REBO and AIREBO are the stiffness of graphene with grain boundaries<sup>20</sup>, carbon nanobelts<sup>21</sup>, load transfer behavior in multi-walled carbon nanotubes (MWNTs) with defects connecting their walls<sup>22-24</sup>, thermal conductivity of C<sub>13</sub> graphene<sup>25</sup>, and the mechanical properties of graphane<sup>26</sup>.

Another member of the graphitic structure family is graphene-oxide (GO). The interest in GO has recently increased because of the discovery of a route to producing pristine graphene from oxidation of graphite<sup>27</sup>. The chemical structure of GO has only recently been revealed<sup>28</sup>, but diverse applications were already considered in flexible electronics<sup>29</sup>, in battery electrodes<sup>30</sup> and as a paper-like composite material<sup>31,32</sup>. We can also expect that graphene produced from graphene oxide through chemical<sup>27</sup> or thermal reduction of oxygen<sup>33</sup>, may partly but not fully inherit the superior thermal conductivity of pristine graphene<sup>34</sup>. The possible oxygen residue on graphene may have strong influence on its thermal conductivity, and this can be studied through equilibrium molecular dynamics simulation<sup>25</sup> as long

as an accurate and computation efficient carbon oxygen many body potential is available for GO. REBO potential formalism meets this requirement. Recent theoretical studies of GO were performed using both Density Functional Theory (DFT)<sup>33,35–37</sup> and ReaxFF<sup>38,39</sup>, but there is no application of the REBO or AIREBO potential to GO. Ni *et al.*<sup>3</sup> have recently extended the second generation of REBO potential<sup>2</sup> to simulate hydrocarbon-oxide molecules. Based on DFT calculations, new parameters were obtained to simulate C–O, O–O, O–H bonds within the REBO formalism, giving rise to a “REBO-CHO” potential. It was originally developed<sup>3</sup> and applied<sup>40,41</sup> to study polymer chains and preliminary tests performed by us demonstrated that REBO-CHO was not suitable to simulate GO. It is important and useful to modify the REBO-CHO potential to be able to optimize its description of GO because it is orders of magnitude more computationally efficient than either ReaxFF or DFT because it lacks explicit treatment of charge.

In this paper, we compare the predictions of DFT and REBO-CHO for oxygen binding energies to graphene, equilibrium C–O bond distances, and other GO properties. We also describe our method for modifying the REBO-CHO potential to provide physical properties of GOs in accordance with DFT, without altering the results for which original REBO-CHO was parameterized. Importantly, we demonstrate that all these issues can be solved by recalculating only the bond order term of the potential.

The paper is organized as follows. In Section II, we present the main expressions of REBO-CHO formalism needed for the reparameterization. In Section III, we show the GO systems used to test REBO-CHO and to provide, from DFT calculations, the binding energies and equilibrium C–O bond distances. We, then, present a list of the discrepancies between REBO-CHO and DFT results. In Section IV, we describe the method for changing REBO-CHO parameters to correctly simulate the physical properties of GOs. We also show some tests performed with the modified REBO-CHO. In Section V, we summarize and discuss the results and conclusions.

## II. REBO-CHO FORMALISM

The *reactive empirical bond order* (REBO) is a classical analytic potential whose name stands for: i) *reactive* means that the potential allows for bonding breaking and forming with appropriate atomic re-hybridization; ii) *empirical* means that its parameters are obtained from fitting to experimental and/or *ab initio* calculation data sets; iii) *bond order* means that the potential explicitly handles the bond-order of a bond in a continuous way.

According to Brenner<sup>42</sup>, a good and effective classical potential for MD simulations should satisfy the following conditions: a) *flexibility*: the potential energy function should accommodate as wide a range as possible of fitting data; b) *accuracy*: the potential should be able to accurately reproduce an appropriate fitting database; c) *transferability*: the potential should be able to describe, at least qualitatively, if not with quantitative accuracy, structures not included in a fitting database; d) *computational efficiency*: the potential should be evaluated for system sizes and timescales of interest in available computing resources. The chemical binding energy potential,  $E_b$ , has the following form:

$$E_b = \sum_i \sum_{j(>i)} [V^R(r_{ij}) - b_{ij}V^A(r_{ij})] , \quad (1)$$

where  $V^R(r_{ij})$  and  $V^A(r_{ij})$  are the pairwise repulsive (core-core and electron-electron) and attractive (core-electron) interaction terms, respectively,  $r_{ij}$  is the distance between nearest-neighbour atoms  $i$  and  $j$ , and  $b_{ij}$  is the bond order term that is a *many-body* function of number and types of neighbors and bond angles. The advantage of this potential is that it well represents the physics and chemistry of a covalent bond, allowing for bond breaking and bond formation in a realistic manner. The main disadvantage is that it cannot treat electronic properties of the system.

The repulsive and attractive interaction terms have the following functional forms:

$$V^R(r) = f^c(r)(1 + Q/r)Ae^{-\alpha r} , \quad (2)$$

and

$$V^A(r) = f^c(r) \sum_{n=1,3} B_n e^{-\beta_n r} , \quad (3)$$

where  $f^c(r)$  is a function used to limit the range of covalent interaction to nearest neighbors,  $r$  is the interatomic distance, and  $Q$ ,  $A$ ,  $B_n$ ,  $\alpha$  and  $\beta_n$  are parameters that are fit to experimental or *ab initio* sets of data. The idea of REBO is that the above interaction terms are corrected by the bond order term:

$$b_{ij} = 0.5[b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi}] + b_{ij}^{\pi}, \quad (4)$$

where  $b_{ij}^{\sigma-\pi}$  and  $b_{ji}^{\sigma-\pi}$  depend on local coordination and bond angles for atom  $i$  and  $j$ , while  $b_{ij}^{\pi}$  depends on dihedral angles for double bonds and whether a bond between atoms  $i$  and  $j$  has radical character and is part of a conjugated system<sup>2,3</sup>. In this work, we will describe how the REBO-CHO was corrected to perform simulations on GOs with the advantage of not modifying its original parameterization.

In the REBO-CHO paper by Niet *et al.*<sup>3</sup>, the parameters and functional forms for C–C, C–H, and H–H interactions were left the same as in the original REBO paper by Brenner<sup>2</sup>. In addition, all of the functional forms used for the extended potential for C–O, O–H, and O–O interactions were also the same as in the original REBO paper by Brenner<sup>2</sup>.  $Q$ ,  $A$ ,  $B_n$ ,  $\alpha$  and  $\beta_n$  that appear in Eqs. (2) and (3) were obtained from a set of few molecules containing the C–O, O–H and O–O bonds. Again, the details of the REBO-CHO full parameterization can be found in REBO-CHO paper by Ni *et al.*<sup>3</sup>. For us, it is important to reproduce the functional form of  $b_{ij}^{\sigma-\pi}$  term:

$$b_{ij}^{\sigma-\pi} = \left[ 1 + \sum_{k(\neq i,j)} f_{ik}^c(r_{ik}) G(\cos(\theta_{ijk})) e^{\lambda_{ijk}} + P_{ij}(N_i^C, N_i^H, N_i^O) \right]^{-\frac{1}{2}}, \quad (5)$$

where indices  $i$ ,  $j$  and  $k$  refer to atoms, the functional  $G(\cos(\theta))$  is an angular function of adjacent bonds (see Refs.<sup>2,3</sup> for details),  $\lambda$  is a fitting parameter designed to describe three-body intermediate states,  $P$  is a bicubic spline function of the quantities  $N_i^C$ ,  $N_i^H$  and  $N_i^O$  that are respectively the number of C, H and O atoms that are the nearest neighbors of atom  $i$ . In fact, in REBO-CHO paper by Ni *et al.*<sup>3</sup>,  $P_{ij} = P_{ij}(N_i^C + N_i^H, N_i^O)$  and is not a function of three parameters as shown in (5), but here we will take advantage of the triple dependence of the spline function on the number of neighbors.

It is through the spline function  $P_{ij}$ , inside the above expression, that allow us to perform a second tuning to account for the C–O bond distances and energies of other molecules as well as setting up non-existing species. By including the knowledge of bond energies of different species, Ni *et al.*<sup>3</sup> were able to compute a full set of spline parameters needed to obtain the spline function (see Table 4 in REBO-CHO paper by Ni *et al.*<sup>3</sup>).

### III. DISCREPANCIES BETWEEN DFT AND REBO-CHO

In order to explain the initial REBO-CHO tests with GO, we first describe the DFT calculations of binding energies and equilibrium C–O bond-distances of different GO species. After that, we present the REBO-CHO results for the same quantities. Then, we summarize the results with a list of the discrepancies between REBO-CHO and DFT calculations.

Total energies were calculated using the Vienna *ab initio* Simulation Package (VASP)<sup>43</sup> with projector augmented wave pseudopotentials<sup>44</sup> for the electron-ion interaction and the local-density approximation<sup>45</sup> for the exchange-correlation functional. The energy cutoff of 500 eV is used for the plane-wave basis expansion. Periodic boundary conditions on graphene plane were considered as well as a 10 Å vacuum region to decouple the interaction between periodic plane images.

In order to avoid confusion, we named the GO systems considered here as follows: 1) “GO-epoxide” is the GO where the oxygen atom binds to two carbon atoms of the graphene forming the so-called *bridge-site* (Fig. 1A); 2) “GO-topsite” is the GO where the oxygen atom binds to just one carbon atom of the graphene, with the C–O bond perpendicular to the original graphene plane (Fig. 1B); 3) “GO-hydroxyl” is the GO where the oxygen of a hydroxyl, OH, is bonded to one carbon atom of graphene, as in the GO-topsite case (Fig. 1C); these three GO systems will be, from now on, referred as “*existing GO species*”; 4) “NEGOS” stands for “*Non Existent Graphene Oxide Species*” according to DFT calculations, like GO–O<sub>2</sub>, GO–H<sub>2</sub>O, GO–OC and others that will be detailed along the text. In this study, we are not considering oxidation of the edges of graphene. Fig. 1 displays the above existing GO species.

Table I presents the binding energies per oxygen and equilibrium C–O bond distances of the three existing GO species calculated with both DFT and REBO-CHO. The binding energies of GO-epoxide and GO-topsite systems can be calculated by the following expression:

$$\Delta E_b = (E_{\text{TOTAL}}(\text{GO}) - E_{\text{TOTAL}}(\text{Graphene})) / (\# \text{ O atoms}), \quad (6)$$

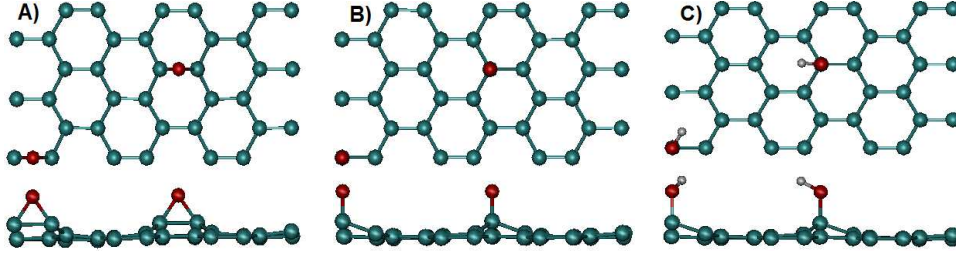


FIG. 1: (Color online) Top and lateral views of existing GO species from DFT calculations. A) GO-epoxide or GO-bridgesite; B) GO-topsite; C) GO-hydroxyl.

TABLE I: Binding energies per oxygen,  $\Delta E_b$ , and equilibrium C–O bond distances,  $d_{\text{C-O}}$ , of GO-species calculated with both DFT and REBO-CHO.

GO species	$\Delta E_b$ - DFT [eV]	$\Delta E_b$ - REBO-CHO [eV]	$d_{\text{C-O}}$ - DFT [Å]	$d_{\text{C-O}}$ - REBO-CHO [Å]
GO-epoxide	-3.18	-5.14	1.44	1.38
GO-topsite	-2.43	-6.74	1.40	1.22
GO-hydroxyl	-1.48	-3.66	1.48	1.35

where  $E_{\text{TOTAL}}(\text{GO})$  and  $E_{\text{TOTAL}}(\text{Graphene})$  are the total energy of the optimized GO and pure graphene structures, respectively. By “optimized” we mean a full 0 K relaxation of the structure, including planar box size optimization. In the case of GO-hydroxyl:

$$\Delta E_b = (E_{\text{TOTAL}}(\text{GO-OH}) - E_{\text{TOTAL}}(\text{Graphene}) - (\# \text{ OHs}) * E(\text{OH})) / (\# \text{ OHs}), \quad (7)$$

where  $E_{\text{TOTAL}}(\text{GO-OH})$  is the total energy of the optimized GO-hydroxyl and  $(\# \text{ OHs})$  is the number of OH groups present in the GO sample.  $E(\text{OH}) = -4.41$  eV is the energy of pure OH.

The discrepancies between DFT and REBO-CHO can be summarized as follows:

1. The binding energies per oxygen calculated with REBO-CHO are, in absolute values, at least 2 eV stronger than those from DFT calculations;
2. Equilibrium C–O bond distances calculated with REBO-CHO are shorter than those from DFT;
3. The most stable GO species according to REBO-CHO is GO-topsite, different from the DFT result that is GO-epoxide.
4. REBO-CHO allows the bond formation of the “NEGOS” structures, as  $\text{GO-O}_2$ ,  $\text{GO-O}_3$ ,  $\text{GO-H}_2\text{O}$ ,  $\text{GO-CO}$ ,  $\text{GO-CO}_2$  and other molecules.

Additionally, the values for the frequency of oscillations of the oxygen atom along some directions of space, from both DFT and REBO-CHO calculations, are presented using the equation  $\omega_{\text{X,Y or Z}} = \sqrt{k_{\text{X,Y or Z}}/m}$ , where  $m$  is the mass of the oxygen atom or OH group, and the force constants  $k_{\text{X,Y or Z}}$  are obtained from static REBO-CHO simulations of the total energy of the GO structure as a function of the C–O distance. Figs. 2 and 3 show good agreement between the DFT and REBO-CHO values for the frequencies of C–O bond oscillation. This result is important because the actual parameterization of REBO-CHO is providing reasonable values for the force constants  $k_{\text{X,Y or Z}}$ , since they are related to the frequencies of the C–O bonds.

#### IV. REPARAMETERIZING REBO-CHO

Instead of performing a full reparameterization of all constants appearing in Eqs. (2) and (3), we followed the idea (as described in Ni *et al.*<sup>3</sup>) of correcting of the bond order term for specific molecules (see Table 4 in Ref.<sup>3</sup>), to address the discrepancies 1 to 4 enumerated in the previous section. We will show that this method not only solves all the discrepancies but also keeps REBO-CHO providing the same results for the original molecules to which it was initially parameterized<sup>3</sup>. Our strategy then is to change the spline function  $P_{ij}$  in order to correct the bond order term only for the C–O bonds where the C belongs to a graphene.

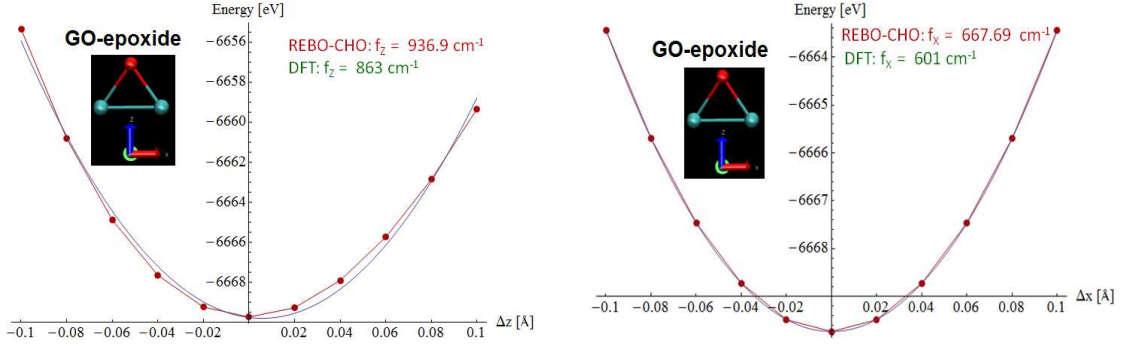


FIG. 2: (Color online) Static energy of GO vs. distance along Z (left) and X (right) directions for the C-O bonds in GO-epoxide system. The calculated frequencies of C-O oscillations with both REBO-CHO and DFT are shown in red and green, respectively. Dots represents MD calculations and the blue line is the best parabolic fitting. Inset shows the local structure and the local system of coordinates.

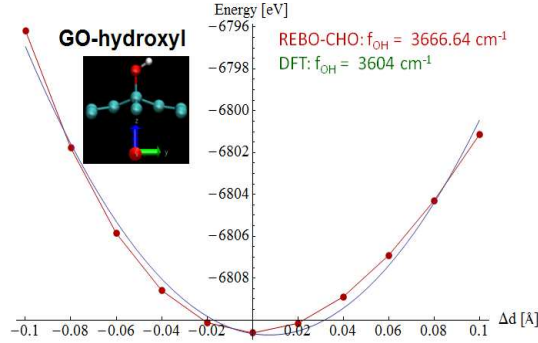


FIG. 3: (Color online) Static energy of GO vs. distance along Z (left) direction for the C-O bonds in GO-hydroxyl system. The calculated frequencies of C-O oscillations with both REBO-CHO and DFT are shown in red and green, respectively. Dots represent MD calculations and the blue line is the best parabolic fitting. Inset shows the local structure and the local system of coordinates.

A good idea of the Brenner potential is relating the bond order to the number of neighbors and to the number of neighbors of the neighbors. We will employ the same idea in our correction of the spline function  $P_{ij}$  in the following way:

$$P_{ij}^{\text{NEW}} = P_{ij} + P_{ij}^{\text{Graphene}}, \quad (8)$$

where  $P_{ij}^{\text{NEW}}$  and  $P_{ij}$  are the corrected and actual spline functions, respectively.  $P_{ij}^{\text{Graphene}}$  represents the amount of correction and the superscript <sup>Graphene</sup> means that this term will be added to the spline function only if the carbon of a C-O bond belongs to the graphene. This can be done in a simple way by testing which atoms are the neighbors of the carbon:

$$P_{ij}^{\text{Graphene}} = \begin{cases} F_{ij}(N_i^C, N_i^H, N_i^O) & \text{if C has at least 3 carbon nearest neighbors.} \\ 0 & \text{if C has 2 or less carbon nearest neighbors.} \end{cases} \quad (9)$$

where  $F_{ij}(N_i^C, N_i^H, N_i^O)$  is a constant that depends on the number of carbon, hydrogen and oxygen neighbors of atom  $i$ :  $N_i^C$ ,  $N_i^H$  and  $N_i^O$ , respectively. Note that  $F_{ij} \neq F_{ji}$  since the neighbors of carbon and oxygen atoms can be different and not always  $b_{ij}^{\sigma-\pi} = b_{ji}^{\sigma-\pi}$ . Therefore, sometimes, we need to adjust both  $F_{ij}$  and  $F_{ji}$  at the same time to fix the discrepancies described in the previous section.

In the next two subsections, we explain the approach we take to fix the discrepancies described in the previous section. Issues numbers 1 to 3 can be fixed in one step, while the issue number 4 needs additional treatment.



### A. Fixing oxygen binding energies to graphene and C–O bond distances

Discrepancies 1, 2 and 3 are related to the oxygen binding energies to graphene and C–O bond distances of existing GO species, namely, the GO-epoxide, GO-topsite and GO-hydroxyl. In order to solve them, the first step is to find out the value of the bond order term,  $b_{\text{C-O}}$ , that gives the right C–O bond energy, which in turn reproduces the desired binding energy according to DFT calculations.

In order to do that, we performed a series of simulations of a given GO sample turning off, in the REBO-CHO code, the calculation of  $b_{\text{C-O}}$  term (i.e., turning off the calculation of Eq. (4) in the code), and manually setting a value for  $b_{\text{C-O}}$ , then relaxing the structure to check if the total energy reaches a desired value. In all simulations reported here, Newton’s equations of motion were integrated with the third-order Nordsieck predictor corrector integration algorithm with the time step of 0.5 fs for a total of 30 ps at 0 K to ensure full optimization. If the chosen value of  $b_{\text{C-O}}$  results in the desired final total energy of the GO, then the value was collected and saved. If not, the value of  $b_{\text{C-O}}$  is changed and the process is repeated in an iterative process until getting the desired final total energy of the GO sample. The same method is repeated for the three existing GO species, saving the  $b_{\text{C-O}}$  of each one. The desired total energy of GO can be calculated using one of Eqs. (6) or (7) where the value of the binding energy per oxygen,  $\Delta E_b$ , is the one obtained from DFT calculations, and the energies of pure graphene and OH molecule are fixed (REBO-CHO already gives correct energies of pure hydrocarbon systems and small oxygen molecules).

The results are presented in Table II, where for the bond order values displayed, the new values of the C–O bond energies given by Eq. (1) are such that the binding energies,  $\Delta E_b$ , of all existing GO species are the same as obtained from DFT calculations with an error at the third decimal place.

TABLE II: Bond order values,  $b_{\text{C-O}}$ , C–O bond energies,  $E_{\text{C-O}}$  (which through Eq. (1) contributes to the calculation of  $\Delta E_b$ ), and equilibrium C–O bond distances,  $d_{\text{C-O}}$ , of existing GO-species from the iteration method described in the text. Last column is for comparison between modified REBO-CHO and DFT results.

GO species	$b_{\text{C-O}}$	$E_{\text{C-O}}$ [eV]	$d_{\text{C-O}}$ [Å]	$d_{\text{C-O}}$ from DFT [Å]
GO-epoxide	0.677669	−2.65	1.45	1.44
GO-topsite	0.716777	−3.01	1.42	1.40
GO-hydroxyl	0.581068	−1.86	1.53	1.48

From the values of the  $b_{\text{C-O}}$  of the existing GO species given in Table II and using Eqs. (4) and (5), we can easily obtain the values for  $F_{ij}$  and  $F_{ji}$  such that the bond order is corrected. Table III presents all values of  $F_{ij}$  and  $F_{ji}$ .

### B. Fixing the formation of “NEGOS”















Discrepancy number 4 is related to the NEGOS structures, i.e., the formation of structures that do not exist according to DFT. These structures are GO–O<sub>2</sub>, GO–H<sub>2</sub>O, GO–O<sub>3</sub>, GO–CO, GO–HO<sub>2</sub> and GO–COH. In order to solve this issue, we follow the same strategy used by Ni *et al.*<sup>3</sup> to avoid non existing species: in the definition of spline function nodes, they obtained the  $P_{ij}$  value in order to take the energy of a C–O bond of a non existing compound to +1.0 eV as a penalty to form such a bond. In order to distinguish this C–O from another one of an existing molecule, the number and type of neighbors of both carbon and oxygen atoms are checked.

Here, based on the neighbors of the oxygen atom of a possible bond between a carbon from graphene and oxygen of a forbidden GO species, we determined values for  $F_{ij}$  and  $F_{ji}$  to make this C–O bond energy equals to +1.0 eV, thus avoiding the formation of this bond. In order to do so, we take Eq. (1) with  $E_b = 1.0$  eV, fix the C–O distance on  $\sim 1.5$  Å, then we obtain the corresponding bond order value, i.e., the value of  $b_{\text{C-O}}$  such that  $E_b = 1.0$  eV. Then using Eqs. (4) and (5) we find out the values of  $F_{ij}$  and  $F_{ji}$  that make  $E_{\text{C-O}} = +1.0$  eV. Table III below presents all values of  $F_{ij}$  and  $F_{ji}$  we have found out to solve all discrepancies between REBO-CHO and DFT, issues from 1 to 4.

In Table III, the C–O bond energy of the GO–OH where the oxygen atom binds to two carbon atoms of graphene (see the GO species number 12 in Table III), was set up to -0.1 eV. It was done because in spite of DFT calculations show no binding energies for that particular structure, it sporadically appears when simulating GO-hydroxyl structures at high temperatures. Setting up a +1.0 eV value for this C–O bond would lead to artificial desorption of hydroxyls from graphene.

Only GO–CO species (not shown on Table III) need an additional treatment because the number and type of nearest neighbors of the oxygen atom in GO–CO is the same as in GO-epoxide, i.e., the oxygen atom of the C<sup>graphene</sup>–O bond has the same number of neighbors  $N^C = 1$  and  $N^H = N^O = 0$  of that of GO-epoxide. Therefore, for the GO–CO species, we perform an additional test: if the carbon atom that is nearest neighbour of the oxygen belongs to the

TABLE III: Values of C–O bond energies,  $E_{\text{C-O}}$ ,  $F_{ji}$  and  $F_{ij}$  for the displayed GO-species. Numbers of carbons,  $N^C$ , hydrogens,  $N^H$ , and oxygens,  $N^O$ , neighbors of the oxygen atom of a C–O bond are shown for clarity.

#	$N^C$	$N^H$	$N^O$	GO species	$E_{\text{C-O}}$ [eV]	$F_{ji}$	$F_{ij}$
1	1	0	0		−2.65	+1.3466	0.0
2	0	0	0		−3.01	+2.3055	0.0
3	0	1	0		−1.86	+7.8131	0.0
4	0	0	1		+1.0	+116.0	+191.24
5	1	0	1		+1.0	+131.0	+108.0
6	1	2	0		+1.0	+60.0	+60.0
7	0	2	0		+1.0	+1300.0	+2240.0
8	0	0	2		+1.0	+1271.0	+14750.0
9	1	0	2		+1.0	+100.0	+85.0
10	2	0	0		+1.0	+131.0	+108.0
11	1	1	1		+1.0	+210.0	+165.0
12	1	1	0		−0.1	+9.0	+2.0
13	2	1	0		+1.0	+116.0	+97.0
14	0	1	1		+1.0	+28648.0	+1098.0

graphene, i.e., if this carbon has three other carbon atoms as nearest neighbors, then it is GO-epoxide and this C–O bond should exist. Otherwise, set the C–O bond energy  $E_{\text{C-O}} = +1.0$  eV. In fact, this test also helps preventing the existence of different “GO–OC...” types of structures.

### C. Tests with GO and non-GO molecules

We also performed finite temperature simulations to test the stability of the GO species. Using original REBO-CHO, GO-topsite is the most stable configuration as it could be seen not only by the value of oxygen binding energy but also by the evolution of GO-epoxide to GO-topsite when performing short simulations at 1500 K or higher temperatures (data not shown). For GO-hydroxyl, when running high temperature simulations (3000 K) with original REBO-CHO, there are no chemical desorptions of OH (data not shown) for which the desorption should be expected<sup>27,28</sup>. It is explained by the fact that original REBO-CHO gives a very strong binding energy of OH to graphene.



After our proposed corrections, we tested the stability of GO-epoxide by performing a series of simulations starting with a GO-top site structure, and increasing the temperature in intervals of 100 K. After 30 ps of MD simulations at high temperatures ( $> 1500$  K), the oxygen atoms started moving from the original top site position to the new, more stable bridge site position. Fig. 4 shows a snapshot of a GO-epoxide after 90 ps of a MD simulation at 3000 K, showing not only the final GO-epoxide configuration but also some desorbed oxygen atoms forming  $O_2$  molecules. This desorption is physically expected to occur<sup>27,28</sup> and did not happen before with the original REBO-CHO because of the strong oxygen binding energies.

With our modified REBO-CHO, OH groups desorbed from graphene at high temperature (data not shown). It qualitatively shows the validity of the correction of the binding energy of OH to graphene when compared to the original REBO-CHO. Nevertheless, a quantitative description of desorption would require the potential to be fitted to the kinetic barriers of desorption.

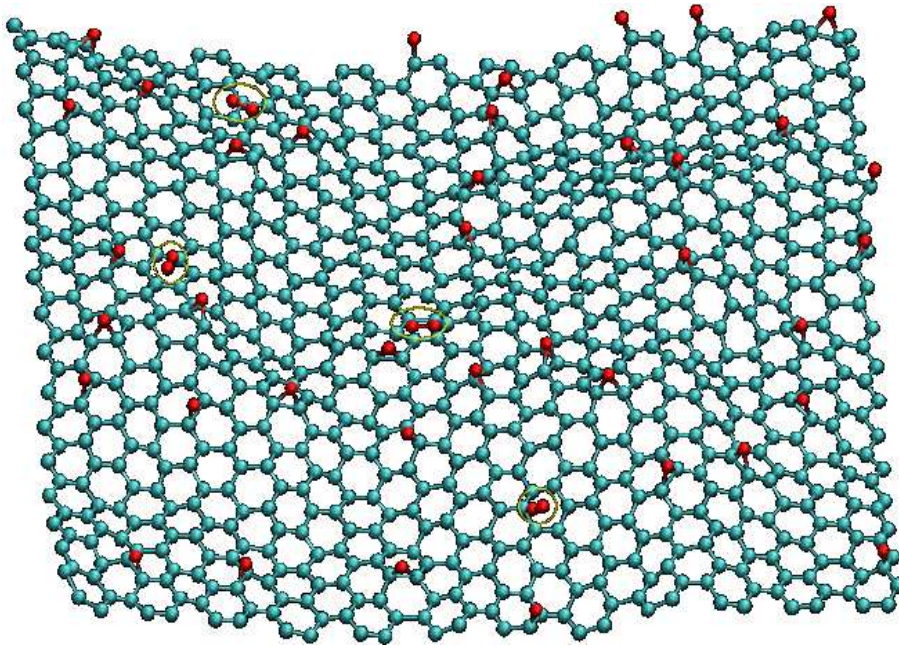


FIG. 4: (Color online) A snapshot of a GO-epoxide structure after 90 ps of a MD simulation at 3000 K.  $O_2$  molecules, marked with yellow circles, form due to desorption of oxygen atoms. The initial structure used for these simulations was the GO-top site, shown in Fig. 1B.

We also tested the existence of NEGOS structures. With the corrections shown in Table III added to REBO-CHO code, none of these structures are formed. As an example, Fig. 5 shows the static energy of frozen graphene and  $O_2$  molecule as a function of distance between them, using both original and our modified parameterization of REBO-CHO. The curve for the original REBO-CHO presents a local energy minimum around  $d_{C-O} \sim 1.3$  Å of distance, while the curve for the modified REBO-CHO presents no local energy minimum, which demonstrates that our correction is now successfully preventing the formation of a chemical bond between a carbon from graphene and an oxygen from the oxygen molecule. The same behavior happens for all other NEGOS structures and curves similar to that of Fig. 5 for the modified REBO-CHO were obtained (data not shown).

Another test was performed with modified REBO-CHO. We estimated the Young's modulus of a monolayer of  $GO-C_{20}O_5H_2$ , i.e., a structure that has 2 hydrogen atoms and 5 oxygen atoms for every 20 carbon atoms, and compared with the recent experimental results by Suk *et al.*<sup>46</sup>. This is an important test because the calculation of the Young's modulus depends on the REBO-CHO results for the total energy of the strained GO. The Young's modulus,  $Y$ , of a structure can be calculated by:

$$Y = \frac{L}{A} \frac{d^2 E}{dL^2}, \quad (10)$$

where  $E$  and  $L$  are the energy and length of the structure, respectively and  $A$  is the cross-sectional area given by  $A = Wt$ , where  $W$  and  $t$  are the width and the thickness of the structure, respectively. The term  $d^2 E/dL^2$  of Eq. (10) is calculated as follows. Ten 0 K simulations of the  $GO-C_{20}O_5H_2$  monolayer were performed where for each

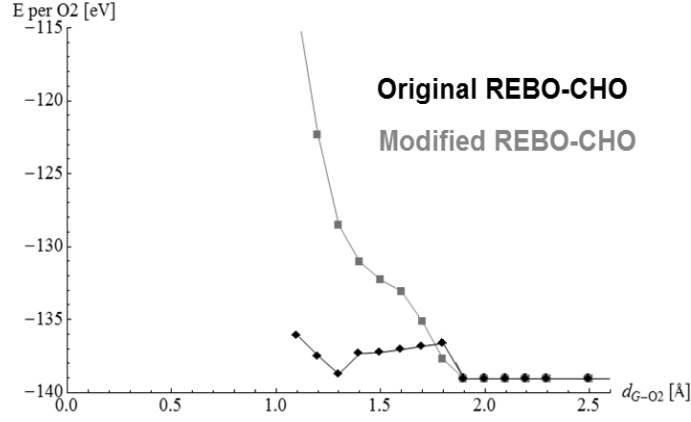


FIG. 5: Static energy of graphene and  $O_2$  molecule vs. distance between them for original (black circle) and modified (gray square) parameterization of REBO-CHO.

simulation, the length of the structure,  $L$ , is varied by  $\pm 0.1$  Å, and the corresponding equilibrium energy  $E$  is taken. By fitting the energy  $E$  as a function of  $L$  by the parabola  $0.5ax^2 + bx + c$ , the Young's modulus can be calculated as

$$Y = \frac{L}{Wt}a. \quad (11)$$

For a  $GO-C_{20}O_5H_2$  monolayer of  $L = 45.76$  Å,  $W = 46.74$  Å and  $t = 7$  Å, where this value of thickness is the same as considered in Ref. <sup>46</sup>, we finally obtained  $Y = 236.8$  GPa, which is in good agreement with the value obtained by Suk *et al*<sup>46</sup>:  $Y = (207.6 \pm 23.4)$  GPa.

The last test is with a non-GO molecule. We compared the results from original and modified REBO-CHO potentials for the atomization energy and C-O bond distances of Tert-butanol molecule ( $C_4H_{10}O$ ). This molecule, illustrated in by Fig. 6, has one carbon atom which form bonds with other three carbon atoms and one oxygen, thus having the same bonding environment of a carbon atom of graphene to which an oxygen atom is bonded. In Fig. 6 we can see some of the bond-distances obtained using original (left) and modified (right) REBO-CHO. The experimental value

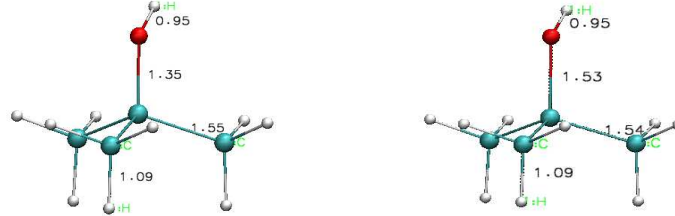


FIG. 6: (Color online) Structure and bond-distances in Å of the  $C_4H_{10}O$  molecule as relaxed by original (left) and modified (right) REBO-CHO.

of the C-O bond distance of the  $C_4H_{10}O$  molecule is  $\sim 1.446$  Å<sup>47</sup>. This value is about the average of the values of the C-O bond-distances obtained with the original and modified REBO-CHO. However, the atomization energy of the  $C_4H_{10}O$  molecule calculated by the modified REBO-CHO potential,  $E = -58.23$  eV, is in much better agreement with the experimental data ( $E = -5534.17$  kJ/mol =  $-57.56$  eV<sup>47</sup>) than that calculated by the original REBO-CHO,  $E = -60.41$  eV. The difference in these energies between original and modified REBO-CHO, is approximately  $\sim 2$  eV, approximately the same discrepancy in the binding energies of oxygen atoms to graphene.

## V. DISCUSSION AND CONCLUSIONS

We have examined the recently extended second generation of REBO potential to include oxygen (REBO-CHO)<sup>3</sup> for molecular dynamics (MD) simulations of GO system. We found discrepancies between REBO-CHO and DFT

results for the oxygen binding energy and C–O bond lengths in GO species. We also found that REBO-CHO is allowing the bond formation of GO and certain molecules as O<sub>2</sub>, CO, among others that according to DFT should not form chemical bonds to graphene.

In order to fix REBO-CHO for MD simulations of GOs, we first calculated the correct values for the bond order term,  $b_{ij}$ , of existing GO species and fixed the C–O bond energies in +1.0 eV for the NEGOS structures. Bond order term controls the bond energy as given by Eq. (1), and the spline function controls the bond order term through Eqs. (4) and (5). We, then added a parameter to the spline function so as to obtain the desired bond order values. This proposed correction of REBO-CHO was shown to fix all discrepancies between REBO-CHO and DFT calculations, making REBO-CHO now suitable to perform MD simulations of GO systems. This would enable REBO-CHO to study mechanical and thermal transport property of GO with good accuracy as well as high computation efficiency. Moreover, the way we modified the REBO-CHO, by Eqs. (8) and (9), does not affect the results of simulations of the molecules for which the potential was originally parameterized. The test with the Tert-butanol molecule, that is a non-GO molecule, showed that the corrected C–O parameters in REBO-CHO will be useful in the study of non-GO molecules where the carbon of the C–O bonds possesses three other carbon neighbors.

To our knowledge, MD simulations of GO systems were performed only with ReaxFF potential<sup>38,39</sup>. Our modified REBO-CHO potential can now be useful for reference and comparison with results from other potentials and experiments as, for example, the Young’s modulus of GO molecules. It can be used to study the atomic structure and mechanical properties of GO with different degree of oxidation with varying amount of epoxide and hydroxyl group coverage at sizes and simulation times much higher than those of existing DFT studies which are very limited due to small system sizes. Besides, the fact that our modifications of REBO-CHO did not reduce its ability to study the systems to which it was originally parameterized, makes our modified potential useful to study systems formed by mixtures of GO and, for example, molecules like amylose, polyoxymethylene (POM) and poly(ethylene terephthalate) (PET). Our MD study will enable the thermodynamic stability study of GO structures even though we may not be able to study the kinetics of GO formation which is yet another challenging modeling problem. A full comparison between ReaxFF and REBO-CHO simulations of general GO systems will be subject of another publication.

Limitations of REBO-CHO for MD simulations of GOs are as follows. Our modifications to the REBO-CHO potential did not include edge oxidation of graphene. According to Gao *et al.*<sup>28</sup>, five- and six-membered lactol rings, ester of a tertiary alcohol and ketone functionalities are formed on the edges of GOs. Our modifications are also not suitable to study the full process of oxidation or burning of graphene because preliminary tests showed that some non existing molecules as CO<sub>3</sub> and CO<sub>4</sub> are allowed to be formed by REBO-CHO when performing very high temperature ( $\gtrsim 3000$  K) simulations of GOs. The reason is that REBO-CHO was originally parameterized to provide correct binding energies of 2(OH)–C=O and C–(OH)<sub>4</sub> molecules<sup>3</sup> which have the feature of having two and three oxygen atoms as nearest neighbors of the carbon of the C–O bond, respectively. It is the same bonding environment of the carbon atom of the C–O bond in CO<sub>3</sub> and CO<sub>4</sub> molecules, respectively. In order to address both the GO edge configurations and the formation of CO<sub>3</sub> and CO<sub>4</sub> molecules, it is necessary to go deeply into the REBO-CHO parameters what can affect the original potential and its validity to simulate the original molecules for which it was parameterized. An example of a full re-optimization of the parameters (including the original parameters for the hydrocarbons) was performed within ReaxFF to study the oxidation of some hydrocarbons<sup>48</sup>. Based on quantum mechanics simulations of a set of bond properties, a new set of ReaxFF parameters were obtained in order to reproduce, at least, the onset of oxidation processes in hydrocarbons. If, on one hand, this reparameterization provided a more accurate potential to simulate the oxidation process of hydrocarbons, on the other hand, the potential loses ability to simulate other physical properties of pure hydrocarbons for which the potential has another set of parameters. In other words, it is a disadvantage to have to rely on different sets of parameters in each type of simulation. In this work, our purpose is to improve the ability to simulate the energy and structure of GO without losing the ability to simulate certain molecules. Therefore, in our case, the issues related to the oxidation of graphene will be left for future work.

### Acknowledgments

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