Probing the accuracy of reactive and non-reactive force fields to describe physical and chemical properties of graphene-oxide

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ABSTRACT: Graphene-oxide (GO) has been shown to be a promising material for numerous technological applications. Extensive computational work has been devoted to elucidate the structure, stability and properties of different GO species. As some applications require large GO sizes, classical molecular dynamics simulations are necessary to fully investigate GO properties

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4 and behavior. There are few classical force fields parameterized to examine oxidized
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6 hydrocarbon compounds, and not all of them are able to simulate GO structures. Here, we
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8 present the first comparative study of some GO properties between three classical force fields:
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10 Reactive Empirical Bond Order for carbon, hydrogen and oxygen (REBO-CHO), third
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12 generation of the Charge Optimized Many Body (COMB3) and Chemistry at HARvard
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14 Macromolecular Mechanics (CHARMM) force field. The chemical and physical properties
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16 tested include key binding energies, carbon-oxygen bond distances and elastic modulus. When
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18 compared to density functional theory calculations or experimental data, the COMB3 reactive
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20 force field is shown to provide the best overall results, while REBO-CHO and CHARMM
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22 provide good results for certain properties of most GO-systems.
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30 Keywords: graphene oxide; molecular dynamics; REBO-CHO; COMB3; CHARMM
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1. Introduction

Graphene oxide (GO) is a widely studied nanostructure and is composed of a graphene sheet functionalized by epoxide and hydroxyl groups on the basal plane, and carboxyl groups at the edges.^[1-3] Recent increased interest in GO comes not only from ease of production,^[4-7] but also from its intriguing physical and chemical properties, which include an open band gap,^[8-10] dispersibility,^[11] thermoelectricity,^[12] giant infrared absorption,^[13] and thermal rectification.^[14] The set of applications that have been considered for GO structures is also wide ranging. It has been shown to be promising for the development of flexible electronics,^[15,16] hydrogen storage,^[17] battery electrodes,^[18] paper materials,^[19] polymer composites,^[20,21] tough foams,^[22] solids,^[23] macroscopic fibers,^[24] adsorbent for toxicity measurements,^[25] gas (water) separation (purification),^[26] and medical therapy applications.^[27,28]

This potential for diverse applications of GO structures can, in principle, be related to the diversity in the number of ways that GO structures may form, as there are an uncountable number of possible combinations of oxygen coverage, epoxide-to-hydroxyl ratio, edge species, as well as the degree of order and/or homogeneity of the oxygen coverage within the graphene basal plane. However, the ability to controllably synthesize different GO structures is still limited. The experimental literature reports the successful synthesis, under different conditions, of the following types of stable GO structures: mixed epoxide and hydroxyl partially oxygen-covered;^[2,5] fully epoxide covered;^[29] and partially hydroxyl-covered in a hydrogen rich environment.^[30] One difficulty that limits the development of well-controlled synthesis routes of GO structures are discrepancies between some theoretical predictions and experimental results. The most important discrepancies are:^[31-35] fully covered GOs are more stable than less covered ones, and hydroxyl groups in GOs are very stable. Some explanations of these discrepancies

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4 have been proposed in terms of kinetic barriers of oxygen diffusion,^[34] free energy
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6 calculations,^[36] and the level of local order in amorphous GOs.^[35] While these solutions have
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8 been proposed based on *ab initio* studies, recently Fonseca *et al.*^[37] proposed that graphene
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10 deformations influence the stability of GO structures and argued that only classical molecular
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12 dynamics (MD) simulations can properly capture these effects on large disordered GO structures.
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14 Encouragingly, their simulation predictions were able to capture most of the experimental
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16 results. This indicates the importance of verified empirical force fields for MD simulations to
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18 provide reliable predictions for GO structures.
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25 Several MD studies that examined the mechanical,^[38,39] thermal,^[40-42] conformational^[43]
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27 and biological^[44] properties of GO structures have been carried to date. For example, Mu and
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29 coworkers^[41] used the original reactive empirical bond order potential of
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31 Carbon/Hydrogen/Oxygen (REBO-CHO).^[45] Other studies^[39,40] used a modified REBO-CHO,^[39]
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33 while still others^[43,44] used the Chemistry at HARvard Macromolecular Mechanics force field
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35 (CHARMM).^[46] More recently,^[38,42] the ReaxFF reactive force field^[47] for hydrocarbon
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37 oxidation (ReaxFF-CHO) was used.^[48] In spite of the importance of these efforts, there are some
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39 issues regarding the validity of some of the force fields used. For example, the original REBO-
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41 CHO^[45] has been shown to wrongly describe the binding energies and bond-distances of carbon-
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43 oxygen atoms in GO.^[39] In addition, a recent report^[49] described the limitations of the ReaxFF-
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45 CHO reactive force field with respect to simulating graphitic structures.
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53 In view of these limitations and the importance to have reliable force fields to simulate
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55 GO structures, we perform a comparative study amongst some of common force fields with
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57 parameters for Carbon/Hydrogen/Oxygen (CHO) systems, in order to determine which ones can
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59 provide reliable predictions regarding the structure, energy and mechanical properties of GO.
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The force fields chosen for this study are the modified REBO-CHO,^[39] CHARMM,^[46] and the third generation of the Charge Optimized Many Body potential (COMB3).^[50] The modified REBO-CHO^[39] was proposed to correctly simulate binding energies and carbon-oxygen (C-O) bond distances of epoxide and hydroxyl species on basal plane of GO structures. It has been successfully applied to the study of energy formation of GO structures with different oxygen concentrations and epoxide-to-hydroxyl ratios.^[37] CHARMM is a force field mainly used to model biological and organic molecules and is widely used. COMB3 has been used to examine metallic,^[51,52] metal oxide,^[53,54] and carbon-based^[55,56] systems, but has not yet been applied to GO materials. A brief description of these force fields is given in Section 2. Although ReaxFF is one of the most known accurate reactive force fields, ReaxFF-CHO was not considered because of the limitation mentioned above for graphitic systems and because we believe that it is just a matter of time before the ReaxFF developers provide new ReaxFF-CHO parameters for GO, as they recently did for condensed phases of carbon.^[49]

Other force fields have been considered to study GO properties and we briefly mention them here. The all-atom optimized potential for liquid simulations (OPLS-AA)^[57] has been used to examine GO behavior in aqueous solutions.^[58-60] Quin and Buehler have combined REBO and CHARMM force-fields to investigate bioinspired folding processes in functionalized graphene.^[61] In addition, Kim *et al.*^[62] have combined different force fields to study the behavior of different gases between GO sheets.

In this work, we defined three tests for the CHO force fields. The first test consists of verifying the agreement between MD and density functional theory (DFT) calculations for the values of binding energy and carbon-oxygen bond distances of regular GO structures having only epoxide or only hydroxyls groups bonded to the basal plane. The second test consists of

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4 verifying the structure and binding energies of four different oxygen edge species to GO
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6 nanoribbons. The third test consists of verifying the agreement of MD simulation predictions
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8 with experimental results, of the elastic moduli of two non-regular GO structures, one with one
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10 layer and the other formed by three layers of a non-regular GO. For the three-layered structure,
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12 we also verified the agreement of the equilibrium interlayer distance with the distance measured
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14 experimentally. Calculated binding energies are important for reactive potentials, as they can
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16 allow for the formation of more stable species through bond breaking or formation in a manner
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18 that is simply related to free energy for GO.^[37] We use the available GO DFT data from the
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20 literature for the comparisons, so other researchers can reproduce the tests directly. The rest of
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22 this paper is organized as follows. In section 2 we describe the force fields considered in this
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24 study, the methods, the set of tests and the structure models. In section 3, we present the results
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26 for each test with corresponding discussion. Lastly, in section 4, we summarize the main results
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28 of this work and present the concluding remarks.
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37 **2. Force fields, methods and tests**

40 *2.1 Force fields.*

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44 The force fields considered in this work are: the modified REBO-CHO,^[39] the
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46 COMB3^[50] and CHARMM.^[46] Each one is defined by a functional of atom positions that is
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48 composed by short-range and long-range terms. Short (long) range terms are responsible for the
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50 chemical (physical) bonding interactions between the atoms within the structure. While the
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52 short-range functional terms differ amongst different force fields, the long-range terms are
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54 similar and based on van der Waals and/or implicit or explicit Coulombic interactions. In what
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56 follows, we briefly describe the short-range characteristics of each force field considered.
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REBO stands for “reactive empirical bond order” and was developed by Brenner *et al.*^[63,64] It is an analytic potential and allows for the dynamical breaking and forming of chemical bonds through the calculation of their corresponding bond order. Its parameters are obtained from either *ab initio* calculations or experimental data and while it was originally developed to model only hydrocarbon structures, it was later extended to model CHO,^[45] CHF,^[65] and CHS^[66] systems. The short-range energy functional in the REBO potential is given by:

$$E_{\text{REBO}} = \sum_i \sum_{j < i} V^R(r_{ij}) - b_{ij} V^A(r_{ij}) , \quad (1)$$

where i, j are indices that run from the first to the last atom of the structure. V^R and V^A are repulsive and attractive terms, respectively, and are functions of each atom pair distance, r_{ij} . b_{ij} is the bond-order term that provides the strength of a given atom pair chemical bond. REBO is considered to be a many-body potential because the calculation of the bond-order of a given i, j pair of atoms depends on their neighborhood and is allowed to change in a continuous and dynamic manner as the atomic positions change. The interested reader is referred to Refs.^[63,64] for more details about the complex functions that make up the bond-order term, b_{ij} .

The original REBO-CHO^[45] was parameterized based on a set of small oxide molecules and chains. It was tested to simulate the structure and properties of amylose, polyoxymethylene (POM), and poly(ethylene terephthalate) (PET) polymers. Later, when tested for the structure and binding energy of epoxide and hydroxyl onto graphene, REBO-CHO was shown to predict much larger binding energies, smaller carbon-oxygen (C-O) bond distances, and non-existing GO species as compared to the results of DFT calculations.^[39] Subsequently, a modified REBO-CHO^[39] was proposed based on a correction of the carbon-oxygen bond-order term, b_{CO} , to obtain, as closely as possible, DFT calculations of the binding energies and C-O bond distances, as well as to prevent CO bond formation of non-existent GO species. The modified REBO-CHO

potential was shown not only to reasonably reproduce the results of DFT calculations, but to also provide good descriptions of the energy formation and stability of different GO systems.^[37]

The third generation of the charge optimized many-body potential,^[50] or COMB3 for short, is a reactive potential based on the calculation of a bond-order parameter as in REBO. But differently from REBO, it has the ability to dynamically calculate and determine the individual equilibrium atomic charges during an MD simulation. It can explicitly handle the electrostatic energy of the system, what is quite important when the system is ionic or contains elements with different electronegativities. In order to do so, COMB adopts a self-consistent dynamically changing charge equilibration approach, in which the charge of each atom is determined by the thermodynamic condition that the electronegativity, defined as the negative value of the electrochemical potential, should be equal at all atomic sites in a closed system at chemical equilibrium.^[67,68] The COMB3 functional is given by:

$$E_{\text{COMB3}} = V^{\text{ES}}(\{r\}, \{q\}) + V^{\text{SHORT}}(\{r\}, \{q\}) + V^{\text{vdW}}(\{r\}) + V^{\text{CORR}}(\{r\}) , \quad (2)$$

where $\{r\}$ and $\{q\}$ represent the set of system atom positions and charges, respectively, and V^{ES} , V^{SHORT} , V^{vdW} and V^{CORR} are the electrostatic, short-range, van der Walls and correction energy terms of the COMB3 force field. COMB3 adopts as V^{SHORT} the same functional given by Eq. (1). The electrostatic term includes the energy of formation of the charge on each atom, charge-charge and charge-nucleus interactions, and atomic polarizability energy terms. The van der Walls energy is given by the classical Lennard-Jones expression^[69] and the correction terms are functions added to prevent the force-field from predicting non-physical or non-chemical processes/species. Many more details of these functional are given in Ref.^[50]

CHARMM is a non-reactive force field developed to describe the energy, structure and thermodynamic properties of biomolecules.^[46] It is formed by bonded and non-bonded terms. The last is composed by van der Walls and Coulombic potentials. The bonded terms form the short-range part of the CHARMM force field and are given by:

$$E_{\text{CHARMM}} = \sum_{\text{bonds}} k_b (b - b_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_\phi [1 + \cos(n\phi - \phi_0)] + \sum_{\text{impropers}} k_\omega (\omega - \omega_0)^2 + \sum_{\text{UB}} k_{\text{UB}} (u - u_0)^2. \quad (3)$$

In sequence, the terms in Eq. (3) account for the dependence of the energy of the chemical bonds on the deviations from the equilibrium values of the bond distance, bond angle, dihedral or torsion angle, improper angle and the so-called Urey-Bradley component that is related to angle bending, respectively. Every term has its respective force constant, k_v , and equilibrium value, v_0 , where v is any of the above variables except for the dihedral term, ϕ_0 , which is a phase shift. Also in the dihedral term, n accounts for the multiplicity of the function.

The main differences between REBO-CHO, COMB3 and CHARMM are the reactivity property and the form of handling the charge distribution and interaction along the simulations. REBO-CHO and COMB3 defines chemical connectivity and hybridization by the relative position of each atom with respect to its atomic neighborhood, and allow for reactions, i. e., bond breaking and formation. CHARMM requires a previous definition of atom connectivity that remains the same during the simulation, despite the amount of displacement that the atoms undergo in response to applied forces. Despite this limitation, CHARMM provides good structural and dynamical properties as long as the atom displacements remain close to the equilibrium values. Amongst these three force fields, only REBO-CHO does not explicitly treat the charge distribution and charge interaction between non-bonded atoms. All of the interactions between the atoms, including electrostatic interactions between electrons, and electrons and

nuclei, are implicitly taken into account in REBO's short-range functional terms. This is enough to describe the structure and properties of a system as long as its chemical bonds are predominantly covalent. CHARMM allows for explicit fixed charge values on each atom and determines the electrostatic interaction between them through a Coulombic energy term. COMB3 not only allows for explicit charge values on each atom and calculates the electrostatic energy between them, it also allows for the dynamic distribution of charge, as explained above.

2.2 Methods.

In this section, we describe the software used to model the GO structures with each force field, the calculation methods employed to obtain the equilibrium structures, and the definitions of the quantities and properties considered.

The modified REBO-CHO is simulated through an MD program that is internal to our group. It has not been made publicly available although it is distributed to individuals on request. This software does not contain minimization algorithms, so in order to reach equilibrium structures, we run an MD simulation within an NVT ensemble, setting the temperature to 0 K with a Langevin thermostat. The MD algorithm integrates Newton's equations of motion with the third-order Nordsieck predictor corrector integration algorithm. We use a time step of 0.5 fs for a total of 30 ps at a minimum, at which point full optimization is reached.

Simulations with COMB3 and CHARMM were carried out using open-source Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package.^[70,71] A conjugate gradient algorithm was employed in all optimizations made with these two force fields.

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4 The REBO-CHO and COMB3 reactive force fields require only structure files with atom
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6 types and well-defined masses as input. Although COMB3 allows for the definition of starting
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8 charges, the process of dynamical charge equilibration will optimize the values of the charges on
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10 each atom according to the system structure. It is therefore acceptable to initially set all the
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12 atomic charges to zero. The connectivity is inferred automatically based on the neighborhood of
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14 each atom. In contrast, CHARMM requires not only a structure file, but also a predefinition of
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16 all force field parameters to run a simulation. In other words, we have to provide all force
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18 constants and equilibrium values in Eq. (3), plus van der Waals parameters. In order to simulate
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20 different GO structures, including GO with different edge species, we selected a few structures
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22 (called *training structures*, which are given in Figure 1) from which we obtain these parameters
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24 through a service provided by the CHARMM General Force Field (CGenFF) program.^[72,73] This
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26 program was created to automate the process of parametrization of molecules for use in classical
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28 molecular mechanics simulations. It performs atom typing and assignment of parameters and
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30 charges by making analogies with an existing database of molecules.^[74,75] By uploading a
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32 *training structure* that possesses the connectivity of the desired structure to be simulated with
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34 CHARMM, the CGenFF program provides the force field parameters and relative charges.
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36 Depending on the structure, some of the terms in Eq. (3) are not required and for these the
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38 CGenFF program gives no parameters. In our case, improper and Urey-Bradley terms were not
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40 necessary to simulate GO. Sometimes, the parameters from the CGenFF program are not free
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42 from errors, but in the absence of other sources of parameters, we nonetheless considered them
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44 here. The van der Waals parameters were taken from Ref.^[61]
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56 Figure 1 shows the *training structures* used to obtain the CHARMM force field
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58 parameters for GO pure epoxide (top left), GO pure hydroxyl (top right), and GO nanoribbons
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with ketone (bottom left), ether (bottom center) and hydroxyl (bottom right) edges. In the supplemental materials we provide the parameters extracted from the CGEnFF program using these molecules. Figures 2, 3 and 4 illustrate the structures of the GOs considered in this work.

Figure 1. Top: two *training* “coronene-like” molecules, $C_{24}H_{12}O$ and $C_{24}H_{12}(OH)_2$, used to obtain CHARMM parameters for simulation of GO pure epoxide and GO pure hydroxyl, respectively. Bottom: three *training* molecules, $C_{56}H_8O_{12}$, $C_{44}H_8O_{12}$ and $C_{56}H_8(OH)_{12}$, used to obtain CHARMM parameters for simulation of GO nanoribbons with ketone (CO), ether (C2O) and hydroxyl (OH) edge oxidations, respectively. Carbon, hydrogen and oxygen are rendered in blue, white and red, respectively.

The main quantities considered in the present study are the binding energy, BE , per oxygen of oxygen-containing species to the graphene structure, C-O bond distance, d_{CO} , and the uniaxial elastic modulus, Y . Binding energies are calculated from one of the following equations:

$$BE_1 = (E_{GO} - E_{GRAPHENE})/\#Os \quad , \quad (4)$$

$$BE_2 = (E_{GO} - E_{GRAPHENE} - E_{OH})/\#OHs , \quad (5)$$

where BE_1 and BE_2 are general formulas to determine the binding energy of pure epoxide and pure hydroxyl GO structures, respectively, from atomic scale calculations or simulations. E_{GO} , $E_{GRAPHENE}$ and E_{OH} are the equilibrium energies, and are determined with each force field, of the GO structure, graphene or “pure carbon structure” and isolated hydroxyl radical, respectively. $\#Os$ ($\#OHs$) is the number of oxygen atoms (hydroxyls) in the GO sample. By “pure carbon structure”, we mean that in the oxide graphene nanoribbon cases, the reference structure for the calculation of the BE is the same ribbon without the oxygen atom species.

The uniaxial elastic modulus is obtained through a series of equilibrium calculations of strained GO structures based on the conjugate gradient algorithm. In each simulation or calculation, the length of the structure is increased by the incremental amount of 0.1% of strain and the equilibrium energy is determined. Furthermore, these energies are fitted by the parabola $0.5aL^2 + bL + c$, where L is the length of the structure. The following expression is used to calculate the elastic modulus:

$$Y = \frac{L}{A} \frac{d^2E}{dL^2} = \frac{L}{Wt} a , \quad (6)$$

where $A = Wt$, with W and t are the cross-sectional area and the width and the thickness of the GO structure. E is the fitted energy function and a is the coefficient of the parabola. A value of thickness of $t = 7 \text{ \AA}$ is taken from Ref.^[76] in order to allow us to compare our results with the experimental value of $Y = (207 \pm 23.4) \text{ GPa}$ for the Young’s modulus of a $GO-C_{20}O_5H_2$.

Although there are several reports on *ab initio* calculations of the mechanical properties of GOs,^[77-80] we prefer to consider the experimental values in view of structure size limitations involving first principles calculations.^[37]

2.3 Tests and structures.

In this section, we describe the three tests carried out with the REBO-CHO, COMB3 and CHARMM force fields in order to evaluate their ability to describe the GO structures and properties. Test 1 consists of the calculation of the binding energy, and C-O bond distance of two GO structures, where each one has a regular distribution of pure epoxide or pure hydroxyl (Figure 2). The values of binding energy of epoxide and hydroxyl to graphene and C-O bond distances are compared to the predictions of DFT calculations of similar structures. Test 2 is about the calculation and comparison to DFT data of the binding energy of the oxygen species and C-O bond distances of four graphene nanoribbons with different edge oxidations (Figure 3). Interest in these structures comes from the known effects of oxygen terminations on the electronic properties of graphene nanoribbons.^[81] Test 3 consists of the calculation of the elastic modulus of a non-regular GO-C₂₀O₅H₂ that is illustrated in Figure 4, a structure with the same oxygen coverage as structures considered experimentally, which facilitates comparison of the potential predictions to experimental results.

Figure 2. Top views of the GO structures ($\sim 50 \text{ \AA} \times 44 \text{ \AA}$) considered in the first test. GO pure epoxide (left) and GO pure hydroxyl (right), both at 5.5% of oxygen coverage, with oxygen species bonded only to one side of the graphene. The color scheme is the same as in Fig. 1.

Figure 3. Top views of small pieces (the total length of the structures is $\sim 46 \text{ \AA}$) of the edge-oxidized graphene nanoribbons considered in Test 2. Edge terminations from left to right: ketone (CO), ether (C_2O), hydroxyl (OH- α) and hydroxyl (OH- β). Hydrogen atoms in OH- α (OH- β) structure are located out of (in) the plane of the ribbon (see lateral views behind the top views of these structures). The color scheme is the same as in Fig. 1.

Figure 4. Top and lateral views of one (top right) and three (bottom right) layers of a non-regular GO- $\text{C}_{20}\text{O}_5\text{H}_2$ structure ($\sim 46 \text{ \AA} \times 46 \text{ \AA}$). The color scheme is the same as in Fig. 1.

3. Results and discussion

3.1 Results of Test 1 – Binding Energies and C-O Bond Distances: GO-Epoxy and GO-Hydroxyl

Table 1 presents the results for the C-O bond distances and binding energies of the structures of Test 1 (Figure 2), calculated with DFT (from Ref.^[39]) and REBO-CHO, COMB3 and CHARMM force fields.

Table 1. Equilibrium bond distances, d_{CO} , and binding energies per oxygen, BE , of epoxide and hydroxyl on graphene. The best matches between DFT and classical force-fields are shown in bold.

	DFT ^{a)}	REBO-CHO	COMB3	CHARMM
GO-epoxide d_{CO} [Å]	1.44	1.45	1.42	1.40
GO-epoxide BE [eV/O]	-3.18	-3.16	-2.88	+1.27
GO-hydroxyl d_{CO} [Å]	1.48	1.53	1.51	1.42
GO-hydroxyl BE [eV/O]	-1.48	-1.41	-1.64	+0.39

a) Ref.³⁹

The oxygen atom in the GO-epoxide structure is predicted to make two bonds to two carbon atoms of graphene that are also chemically bonded. One important test for the force fields, not presented in Table 1, is the distance between these two carbon atoms. This distance has been experimentally measured to be about 1.514 Å,^[82] larger than in pristine graphene as a consequence of the sp^3 hybridization character of the bond. The REBO-CHO, COMB3 and CHARMM force fields predict values of 1.61 Å, 1.63 Å and 1.53 Å for the equilibrium distances of the carbon-carbon bonds behind the epoxide species, respectively. REBO-CHO and COMB3

provide good results, defined here to have errors within ~ 0.1 Å. CHARMM provided a result in excellent agreement with the experiments.

3.2 Results of Test 2 – Binding Energies and C-O Bond Distances: Edge-Oxidized Graphene Nanoribbons

Tables 2 and 3 present the results for the binding energy and C-O bond distance of the structures of Test 2 (Figure 3), respectively, calculated with DFT and REBO-CHO, COMB3 and CHARMM potentials. Here, the binding energy DFT data was taken from Ref.^[83], and the DFT bond distances were taken from Ref.^[84] and from the Computational Chemistry Comparison and Benchmark DataBase (CCCBDB)^[85] for the organic molecules phenoxy-radical, tetrahydrofuran and phenol, chosen because they have similar carbon-oxygen terminations as those of graphene nanoribbons with ketone (CO), ether (C₂O) and hydroxyl (OH), respectively. As some discrepancies appeared in the binding energy calculations between all the force fields and DFT results of Ref.^[83], we also estimated the binding energy of oxygen to those small organic molecules from CCCBDB data obtained with DFT calculations using the hybrid B3LYP method with the 6-311G* basis set. The binding energies of oxygen and hydroxyl in phenoxy-radical and phenol molecules, respectively, were calculated with respect to the energy of phenyl molecule. The binding energy of oxygen in the tetrahydrofuran molecule was calculated with respect to the energy of the cyclobutane molecule.

Table 2. Binding energy per oxygen, in (eV/O), of four different oxygen edge-terminations in graphene nanoribbons. The best matches between DFT and classical force-fields are highlighted in bold. The same trend in the binding energy values of hydroxyl (OH- α) and (OH- β) graphene nanoribbons as in Ref.⁸³ is highlighted in *italic* font.

Edge-termination	DFT	REBO-CHO	COMB3	CHARMM
ketone (CO)	-8.00 ^{a)} , -5.51 ^{b)}	-8.19	-5.38	+1.81
ether (C2O)	-9.09 ^{a)} -4.69 ^{b)}	-7.68	-8.14	+0.39
hydroxyl (OH- α)	-8.05 ^{a)}	-4.94	-4.88	- ^{c)}
hydroxyl (OH- β)	-8.93 ^{a)} , -4.66 ^{b)}	-4.58	-4.91	+0.79

^{a)} Ref.⁸³

^{b)} Data for small organic molecules obtained from Ref.⁸⁵

^{c)} CHARMM did not present a planar equilibrium solution for graphene nanoribbon with hydroxyl (OH- α) termination.

Table 3. Equilibrium bond distance, in Å, of four different oxygen edge-terminations in graphene nanoribbons. The best matches between DFT and classical force-fields are shown in bold.

Edge-termination	DFT	REBO-CHO	COMB3	CHARMM
ketone (CO)	1.23 ^{a)} , 1.25 ^{b)}	1.21	1.32	1.23
ether (C2O)	1.43 ^{b)}	1.36	1.40	1.38
hydroxyl (OH- α)	1.37 ^{b)}	1.33	1.43	- ^{c)}
hydroxyl (OH- β)	1.37 ^{b)}	1.33	1.44	1.42

^{a)} Ref.⁸⁴

^{b)} Data for small organic molecules obtained from Ref.⁸⁵

^{c)} CHARMM did not present a planar equilibrium solution for graphene nanoribbon with hydroxyl (OH- α) termination.

3.3 Results of Test 3 – Elastic Moduli of GO- C₂₀O₅H₂ Structures

Table 4 presents the results for the uniaxial elastic modulus of non-regular GO-C₂₀O₅H₂ structures with one and three layers, and the experimental result is from Ref.^[76] The elastic modulus was calculated using Eq. (6) and $t = 7(21)$ Å as thickness for one(three) layered structure.

Table 4. Elastic modulus (in GPa) of non-regular GO-C₂₀O₅H₂ structures with one and three layers. The best matches between experimental and classical force-fields are highlighted in bold.

Number of layers	Experiment ^{a)}	REBO-CHO	COMB3	CHARMM
1	207.6 ± 23.4	206.9	161.1	204.3
3	229.5 ± 27.0	645.7	167.2	409.6

^{a)} Effective Young's modulus, Ref.^[76]

The interlayer distance in the three-layered non-regular structure of GO-C₂₀O₅H₂ was also compared to experimental results. An experimental work on hydration of bilayered GOs^[86] shows that in the limit of low humidity, the distance between two layers of GO goes to $\sim < 0.7$ nm (see Figure 2 of Ref.^[86]). From the simulations performed here with REBO-CHO and COMB3, we obtained 0.67 nm and 0.32 nm for the equilibrium interlayer distance at null humidity, respectively.

3.4 Discussion.

From the results in Table 1, we verified that REBO-CHO and COMB3 force fields provide excellent binding energies of oxygen species to graphene and good C-O bond distances. The results for the REBO-CHO are not surprising since it was parameterized to match the DFT binding energy and C-O bond distance calculations. However, it is useful to note that COMB3, which did not include GO in its parameterization, does quite well in the predictions of these

chemical and structural properties of GOs. COMB3 is even better than REBO-CHO for the C-O bond distance in GO-hydroxyl. The CHARMM force field provided good C-O bond distances as compared to DFT but cannot capture the binding energies of oxygen species to graphene. This is not a significant problem for CHARMM, since it cannot be used to simulate reactions. We note that it is beyond the scope of this work, to provide more precise CHARMM force field parameters and the good results from CHARMM illustrate its power to model many properties of GOs. All three of the force fields considered predict good results for the test of the distance between the carbon atoms just “behind” the oxygen in GO-epoxide. This is an important test because experimental results show no breaking of this bond for isolated epoxide.

Table 2 illustrates some discrepancies in the calculated binding energies between some of the force fields considered and the predictions of DFT calculations. This and the lack of information regarding the values of C-O bond-distances in Ref.^[83] motivated us to perform an additional test by calculating the binding energy and C-O bond distance of some small organic molecules that possess similar oxygen terminations as those of our oxidized graphene nanoribbons. For the same reason as in Test 1, the CHARMM results of binding energy are not optimal and are therefore not taken into account in this analysis. The discrepancies between the force field and DFT results for the binding energy occurred for graphene nanoribbons with hydroxyl terminations, and were larger than 3 eV. For graphene nanoribbons with ketone (CO) terminations, REBO-CHO presented the best match with DFT calculations. However, COMB3 provided a good match to the DFT determination^[85] of binding energy of oxygen atoms to the phenyl group in a phenoxy-radical molecule. For graphene nanoribbons with ether (C₂O) termination, COMB3 provided the best match to the predictions of DFT calculations^[83] of the binding energy of oxygen to the structure. For the hydroxyl (OH) terminated graphene

nanoribbons, the REBO-CHO and COMB3 values of binding energy of OH to the structure are close to that of OH to phenyl in phenol molecule, with REBO-CHO providing the best match, although COMB3 did not provide values that are substantially different. One interesting remark made by the authors of Ref.^[83] is that the binding energy of OH to the graphene nanoribbon structure in OH- α structure is smaller than that in OH- β structure or, $BE_{OH-\alpha} < BE_{OH-\beta}$. This occurs due to the fact that in OH- β structure, hydrogen bonding forms between the hydrogen atom at one hydroxyl to the oxygen atom of an adjacent hydroxyl. COMB3 was the only one force field that captured this trend as highlighted in *italic* in Table 2.

Regarding the bond distances in the edge-oxidized graphene nanoribbons, as indicated in Table 3, CHARMM and REBO-CHO predicted excellent values for the ketone (CO) edge-termination, while the best match for the ether (C₂O) termination was provided by COMB3. Although REBO-CHO provided the best values for the C-O bond distances in the hydroxyl (OH) graphene nanoribbons, COMB3 and CHARMM provided good values as well. CHARMM failed to provide a planar equilibrium solution for the graphene nanoribbon with hydroxyl (OH- α) terminations.

The elastic modulus of non-regular GO-C₂₀O₅H₂ structures with one and three layers are presented in Table 4. REBO-CHO and CHARMM provided very good determinations for the elastic modulus of one layer GO in comparison to experimental results, although COMB3 result is also reasonable. For the three-layered structure, however, the results are different and also differ from the experimental value. REBO-CHO and CHARMM predict a much stiffer result, while COMB3, although providing the smallest value, amongst the force fields considered here, displayed a trend for the stiffness of the one-layered and three-layered structures that is in good

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4 agreement with the experimental results. The similarity between the values of the elastic
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6 modulus for these GO structures was explained in terms of the existence of strong bonding
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8 between the layers in the three-layered case,^[76] which prevents interlayer sliding. It is therefore
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10 interesting to note that the equilibrium interlayer distance of 0.32 nm obtained with COMB3,
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12 although not in good agreement with the findings of another experiment,^[86] gives support to this
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14 conclusion since at a small interlayer distance, the interaction among the layers are larger and
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16 stronger than that at longer interlayer distances. COMB3 is, then, the only force field which
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18 predicted the same similarity in the values of the elastic modulus of the one-layered and three-
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20 layered GO structures.
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25 26 27 **4. Conclusions** 28 29

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31 We have performed a set of comparative tests of predictions of some chemical and
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33 physical properties of GO structures amongst three commonly used force fields, namely REBO-
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35 CHO, COMB3 and CHARMM. While the REBO-CHO and CHARMM force fields were shown
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37 to provide excellent predictions of some of the properties studied here, COMB3 was shown to
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39 present overall good predictions for almost all properties, and is considered to be the best choice
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41 for the investigation of physical and chemical properties of different GO structures among the
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43 three force fields considered. An additional advantage of the COMB3 force field is its
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45 availability to the technical community through the open-source LAMMPS software and the fact
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47 that it does not require the pre-definition of atomic connectivity and initial atomic charges.
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53 With the increased interest in the development of large systems formed by GO
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55 structures,^[20-24] the importance of good computational tools for the prediction of the properties of
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57 these materials is timely. Our tests illustrate the usefulness and the limits of validity of REBO-
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4 CHO, COMB3 and CHARMM force fields for simulations of GO structures. In terms of relative
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6 speed, if $\langle t_{\text{FORCE FIELD}} \rangle$ is the time of duration of a complete MD simulation of a given GO
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8 structure run for the same total number of steps on a given computational cluster and subjected to
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10 the same conditions, $t_{\text{COM3}} > t_{\text{REBO-CHO}} > t_{\text{CHARMM}}$. This is because CHARMM is not reactive,
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12 REBO-CHO is reactive and many body but does not include dynamic charge, and COMB3 is
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14 reactive, many body, and includes dynamic charge. The choice of force field to perform a given
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16 MD simulation may need to consider computational cost as a factor, especially for very large
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18 systems.
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25 Although some studies of the interaction between water and GO structures have been
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27 made with non-reactive CHO force fields,^[58-60] the possibility of reactions and charge
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29 equilibration might be important in applications such as graphene-membrane^[87] or for GO in the
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31 presence of confined water.^[88] Additionally, the similarity of the results for the binding energy
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33 and C-O bond distances with those of the phenoxy-radical, tetrahydrofuran and phenol molecules
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35 indicates that these potentials are also good choices for the study of oxidized polyaromatic
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37 carboxylated fragments, or oxidative debris, in GO structures^[89] and acidic and basic surface
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39 functionalities on carbon basal planes in activated carbon.^[90]
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49 **Supplementary material.** Additional supplementary material can be found in the online version
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51 of this article.
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55 **Acknowledgments**
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