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

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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 have been proposed in terms of kinetic barriers of oxygen diffusion [34], free energy calculations [36], and the level of local order in amorphous GOs [35]. While these solutions have been proposed based on *ab initio* studies, recently Fonseca et al. [37] proposed that graphene deformations influence the stability of GO structures and argued that only classical molecular dynamics (MD) simulations can properly capture these effects on large disordered GO structures.

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Encouragingly, their simulation predictions were able to capture most of the experimental results. This indicates the importance of verified empirical force fields for MD simulations to provide reliable predictions for GO structures.

Several MD studies that examined the mechanical [38,39], thermal [40–42], conformational [43], and biological [44] properties of GO structures have been carried to date. For example, Mu and coworkers [41] used the original reactive empirical bond order potential of Carbon/Hydrogen/Oxygen (REBO-CHO) [45]. Other studies [39,40] used a modified REBO-CHO [39], while still others [43,44] used the Chemistry at HARvard Macromolecular Mechanics force field (CHARMM) [46]. More recently [38,42], the ReaxFF reactive force field [47] for hydrocarbon oxidation (ReaxFF-CHO) was used [48]. In spite of the importance of these efforts, there are some issues regarding the validity of some of the force fields used. For example, the original REBO-CHO [45] has been shown to wrongly describe the binding energies and bond-distances of carbon–oxygen atoms in GO [39]. In addition, a recent report [49] described the limitations of the ReaxFF-CHO reactive force field with respect to simulating graphitic structures.

In view of these limitations and the importance to have reliable force fields to simulate GO structures, we perform a comparative study among some of common force fields with parameters for Carbon/Hydrogen/Oxygen (CHO) systems, in order to determine which ones can provide reliable predictions regarding the structure, energy and mechanical properties of GO. 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 verifying the structure and binding energies of four different oxygen edge species to GO nanoribbons. The third test consists of verifying the agreement of MD simulation predictions with experimental results, of the elastic moduli of two non-regular GO structures, one with one layer and the other formed by three layers of a non-regular GO. For the three-layered structure, we also verified the agreement of the equilibrium interlayer distance with the distance measured exper-

imentally. Calculated binding energies are important for reactive potentials, as they can allow for the formation of more stable species through bond breaking or formation in a manner that is simply related to free energy for GO [37]. We use the available GO DFT data from the literature for the comparisons, so other researchers can reproduce the tests directly. The rest of this paper is organized as follows. In Section 2 we describe the force fields considered in this study, the methods, the set of tests and the structure models. In Section 3, we present the results for each test with corresponding discussion. Lastly, in Section 4, we summarize the main results of this work and present the concluding remarks.

2. Force fields, methods and tests

2.1. Force fields

The force fields considered in this work are: the modified REBO-CHO [39], the COMB3 [50] and CHARMM [46]. Each one is defined by a functional of atom positions that is composed by short-range and long-range terms. Short (long) range terms are responsible for the chemical (physical) bonding interactions between the atoms within the structure. While the short-range functional terms differ among different force fields, the long-range terms are similar and based on van der Waals and/or implicit or explicit Coulombic interactions. In what follows, we briefly describe the short-range characteristics of each force field considered.

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:

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

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].