# Can force fields developed for carbon nanomaterials describe the isomerization energies of fullerenes?

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# ABSTRACT

We evaluate the performance of carbon force fields for 1811 C<sub>60</sub> PW6B95-D3/Def2-QZVP isomerization energies. Several force fields (most notably the machine-learning GAP-20 potential) exhibit a high statistical correlation with the DFT isomerization energies. Therefore, linear scaling of the isomerization energies can significantly improve the accuracy. The best scaled force fields attain mean-absolute deviations of 8.5 (GAP-20), 12.3 (LCBOP-I and REBO-II), and 13.3 (ABOP) kcal mol<sup>-1</sup>, which translate to mean-absolute relative deviations of 4.7% (GAP-20), 6.5% (LCBOP-I), 6.6% (REBO-II) and 7.1% (ABOP). Therefore, these force fields offer a computationally economical way for exploring the relative energies of fullerenes.

Keywords: Force fields; Interatomic potentials; Machine-learning; Fullerenes; Isomerization energies.

#### Cite as:

A. Aghajamali, A. Karton. Can force fields developed for carbon nanomaterials describe the isomerization energies of fullerenes? *Chem. Phys. Lett.*, 779, 138853 (2021). https://doi.org/10.1016/j.cplett.2021.138853

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### Introduction

Predicting the relative energies of fullerenes and carbon nano-onions is an important area of computational nanotechnology.<sup>1,2,3,4,5,6,7,8</sup> These carbon nanostructures typically involve hundreds or even thousands of carbon atoms, and thus their relative energies cannot normally be calculated by means of density functional theory (DFT) procedures. Molecular mechanics is the fastest and conceptually simplest method for calculating structural properties of large nanomaterials. Molecular mechanics also provides a practical avenue for running long-timescale molecular dynamics (MD) simulations which are of key importance in studying the dynamic behavior of carbon nanomaterials. Indeed, molecular mechanics is extensively used for studying the structural and dynamic properties of nanomaterials.

A large number of interatomic potentials have been specifically developed for carbon nanomaterials.<sup>9,10,11,12</sup> (For an historical perspective of carbon potentials and in-depth discussion of the merits of dominant models see also ref. 13.) An exciting recent development in this area is the development of machine-learning based potentials.<sup>14</sup> The interatomic potentials have been extensively benchmarked for a wide range of physical, thermal, and chemical properties of carbon nanostructures (e.g., elastic moduli, bond angle distributions, radial distribution functions, and structural, and phase-transition properties).<sup>10,11,15,16,17,18,19,20,21,22</sup> However, less attention has been given to benchmarking relative energies of fullerenes and nanotubes, which are key reference materials for the validation and parameterization of density functional and semiempirical molecular orbital (SMO) theories. In an extensive benchmark study, Sure *et al.*<sup>1</sup> recently calculated the isomerization energies for the entire set of 1812 isomers with the hybrid-meta generalized gradient approximation (GGA) PW6B95-D3 functional in conjunction with the Def2-QZVP basis set. In the present work, we use these benchmark values to evaluate the performance of a wide range of commonly used carbon interatomic potentials for the relative energies of the entire set of 1812 C<sub>60</sub> isomers. Importantly, since none of the considered

potentials were parameterized for isomerization energies of carbon nanostructures, this test set represents a difficult and completely independent measure of the ability of the carbon potentials to model energetic properties of nanostructures. Two important findings are that (i) all carbon force fields tend to systematically underestimate the C<sub>60</sub> isomerization energies, and (ii) several force fields exhibit a high statistical correlation with the PW6B95-D3/Def2-QZVP isomerization energies (most notably the machine-learning GAP-20 potential for which  $R^2 = 0.962$ ). Therefore, we show here that linear scaling of the isomerization energies results in high accuracy relative to computational cost for the carbon potentials for which both of these points apply.

#### **Computational details**

All the reference isomerization energies (calculated at the PW6B95-D3/Def2-QZVP level of theory) and reference structures for the C<sub>60</sub> isomers (optimized at the PBE-D3/Def2-TZVP level of theory)<sup>23,24,25</sup> which are used in the present work are taken from Ref. 1. For brevity the PW6B95-D3/Def2-QZVP//PBE-D3/Def2-TZVP level of theory will be denoted by PW6B95-D3/Def2-QZVP hereinafter. We note that, for the five energetically most stable C<sub>60</sub> isomers and five higher-energy isomers with energies of up to 166 kcal mol<sup>-1</sup>, Ref. 1 obtained domain based local pair natural orbital coupled-cluster energies with single, double, and quasiperturbative triple excitations (DLPNO-CCSD(T))<sup>26</sup> close to the complete basis set (CBS) limit.<sup>27</sup> For this set of nine isomerization energies the PW6B95-D3/Def2-QZVP level of theory attains a mean absolute deviation (MAD) of 1.6 kcal mol<sup>-1</sup> relative to the DLPNO-CCSD(T)/CBS reference values.<sup>1</sup> These results indicate that the PW6B95-D3/Def2-QZVP reference isomerization energies should be sufficiently accurate for benchmarking carbon potentials. In addition, it should be pointed out that the PW6B95-D3/Def2-QZVP

isomerization energies have been used in Ref. 1 to benchmark several semiempirical methods (*vide infra*).

Here, we use the PW6B95-D3/Def2-QZVP relative energies for the 1812 C<sub>60</sub> isomers for benchmarking a wide range of carbon potentials. In particular, we examine the following twelve common carbon interatomic potentials:

- ⇒ The Tersoff potential was parameterized against experimental data such as the lattice constants and binding energies of diamond and graphite, in addition to C–C bond energies obtained from DFT calculations.<sup>28</sup> Tersoff-S is a screened version of the Tersoff potential in which an environment-dependent function is added for improving the description of bond breaking/making processes.<sup>29</sup>
- $\Rightarrow$  The environment-dependent interaction potential (EDIP) was developed to simulate the growth of amorphous carbon thin film and liquid quenched carbon systems, in addition to DFT bond energies involved in the graphite-to-diamond transition.<sup>30</sup>
- ⇒ The second generation of REBO potential (REBO-II) is an extended version of the Tersoff potential, in which the description of short-range bonding is improved by modifying the functional form. The potential parameters were fitted to experimental binding energies and lattice constants of graphite and diamond, and DFT binding energies and lattice constants of simple cubic and face-centered cubic phases of carbon.<sup>31</sup> In the screened REBO-II potential (REBO-II-S), the description of bond-making/breaking is improved by adding an environment-dependent function.<sup>32</sup>
- ⇒ The adaptive intermolecular reactive empirical bond order (AIREBO) potential is based on the REBO-II potential and includes a Lennard–Jones switching function for inactivating the long-range terms at short distances.<sup>33</sup> The AIREBO-M potential is a modified version of AIREBO in which the Lennard–Jones term is replaced with a Morse-type expression.<sup>34</sup>

- $\Rightarrow$  The long-range carbon bond order potential (LCBOP-I) is similar to the AIREBO potential and is developed to improve the accuracy and transferability of the model by reparameterization of the bond order potential. The parameters are obtained from the REBO potential and DFT calculations.<sup>35</sup>
- $\Rightarrow$  Zhou *et al.* developed a variant of the analytic bond-order (ABOP) potential for carbon based on the previous versions of this potential,<sup>36</sup> which was developed from a quantum mechanical tight-binding model.<sup>37</sup>
- ⇒ The ReaxFF potential is a bond-order potential developed by Duin *et al.*<sup>38</sup> The reparametrized version of ReaxFF (denoted here by ReaxFF-15) was developed for improving the solid carbon phase using a large dataset of DFT-D2 structures including small fullerenes and different amorphous carbon phases.<sup>39</sup> ReaxFF-20 is a reparametrized version of the ReaxFF potential,<sup>40</sup> optimized to adequately capture the flattened carbon nanotube structure and the corresponding energy values using PCFF-IFF force-field data, which agrees well with DFT-D2 data.<sup>41</sup>
- $\Rightarrow$  In the recently developed Gaussian approximation potential (GAP-20), kernel-based machine learning is employed instead of the classic empirical form, and the potential was fitted against reference data calculated with the optB88-vdW DFT method.<sup>42</sup>

The force-field C<sub>60</sub> isomerization energies were calculated using both the PBE-D3/Def2-TZVP reference geometries from Ref. 1 and geometries optimized with each of the force fields. In the latter geometry optimizations, the energy of the C<sub>60</sub> isomers was minimized using a conjugate gradient scheme. All calculations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package.<sup>43,44</sup>

### **Results and discussion**

*Performance of interatomic potentials for the relative energies of 1812 C<sub>60</sub> isomers.* The energetically most stable C<sub>60</sub> isomer is of course the well-known  $I_h$  symmetry buckminsterfullerene. The highest energy C<sub>60</sub> isomer lies 549.1 kcal mol<sup>-1</sup> above the buckminsterfullerene structure at the PW6B95-D3/Def2-QZVP level of theory and has a nanorod-shaped structure with  $D_{5d}$  symmetry (Figure 1). Thus, the 1811 reference isomerization energies span over a very wide energetic window with an average isomerization energy of 189.8 kcal mol<sup>-1</sup>. Nevertheless, as pointed out in Ref. 1, most of the isomers (namely, 70%) span a narrower energetic range of 150–250 kcal mol<sup>-1</sup>. For a detailed discussion of the isomer distribution see Ref. 1.



Most stable C<sub>60</sub> isomer I<sub>h</sub>, 0.0 kcal/mol



Least stable C<sub>60</sub> isomer D<sub>5d</sub>, 549.1 kcal/mol

**Figure 1.** Optimized PBE-D3/Def2-TZVP structures of the most and least energetically stable C<sub>60</sub> isomers. The point-group symmetry and the relative PW6B95-D3/Def2-QZVP isomerization energies are also given.

Figure 2 depicts the correlation between the force field and PW6B95-D3/Def2-QZVP isomerization energies for all the carbon potentials. The force field isomerization energies are calculated (i) on top of the PBE-D3/Def2-TZVP geometries used for calculating the PW6B95-D3/Def2-QZVP reference isomerization energies, and on top of geometries optimized with

each of the force fields. Inspection of Figure 2 reveals that in some cases (e.g., GAP-20, ReaxFF-15, and ReaxFF-20) reoptimizing the PBE-D3/Def2-TZVP reference geometries with each of the force fields has a relatively small effect on performance, whilst in other cases (e.g., AIREBO, AIREBO-M, REBO-II-S, Tersoff-S, and EDIP) reoptimizing the reference geometries with each of the force fields results in a visual deterioration in performance. In the latter cases, reoptimizing the geometries makes the underestimation of the isomerization more pronounced. A natural question that arises is, what is the effect of reoptimizing the structures with a given carbon potential on its performance for the C60 isomerization energies? Table S1 of the Supporting Information lists the MADs relative to the PW6B95-D3/Def2-QZVP C60 isomerization energies. Inspection of these results reveals that reoptimizing the geometry generally leads to deterioration in performance, however, the effect of reoptimizing the geometry can vary significantly between the various carbon potentials. In particular, reoptimizing the geometry increases the MADs by relatively small amounts of 2–5 kcal mol<sup>-1</sup> (for ReaxFF-15, ReaxFF-20, and GAP-20) and up to 75 kcal mol<sup>-1</sup> for Tersoff-S (Figure 2 and Table S1). Hereinafter, the main text considers the performance of the carbon potentials using the PBE-D3/Def2-TZVP geometries, whilst the results for the force-field optimized geometries are given in the Supporting Information.



**Figure 2.** Correlation between the PW6B95-D3/Def2-QZVP isomerization energies and the force-field isomerization energies calculated using the PBE-D3/Def2-TZVP geometries (colored points) and the structures optimized with each of the force fields (gray points).

Table 1 gives the error statistics for all the carbon potentials for the relative energies of the 1812 C<sub>60</sub> isomers. The MADs clearly show that the GAP-20 machine-learning potential significantly outperforms the conventional (empirical) potentials with a MAD of 29.5 kcal mol<sup>-1</sup>, which translates to a mean-absolute relative deviation of 16.0%. It should be pointed out that the GAP-20 carbon potential gives similar performance to the best SMO-based methods considered in Ref. 1, which attain MADs of 28.1 (PM6-D3) and 31.0 (PM7) kcal mol<sup>-1</sup>. The second-best potential (Tersoff-S) attains a MAD of 40.0 kcal mol<sup>-1</sup>, which translates to a mean-absolute relative deviation of 40.0 kcal mol<sup>-1</sup>, which translates to a mean-absolute relative deviation of 40.0 kcal mol<sup>-1</sup>, which translates to a mean-absolute relative deviation of 40.0 kcal mol<sup>-1</sup>, which translates to a mean-absolute relative deviation of 20.1%. Again, it should be pointed out that this carbon potential gives outperforms some of the SMO-based methods considered in Ref. 1, which attain MADs

of 41.9 (OM2-D3) and 57.0 (AM1) kcal mol<sup>-1</sup>. The other carbon potentials attain large MADs ranging between 62.7 (REBO-II) and 127.6 (EDIP) kcal mol<sup>-1</sup> and are thus of limited quantitative applicability in the context of the C<sub>60</sub> isomers. The mean signed deviations (MSDs) in Table 1 show that nearly all the carbon potentials systematically underestimate the isomerization energies (i.e.,  $MSD = -1 \times MAD$ ). Interestingly, Tersoff-S is the only potential for which some of the isomerization energies are overestimated (Figure 2 and Table 1). In addition, it is important to note that the machine-learning formalism in the GAP-20 potential reduces the bias towards underestimation (Figure 2 and Table 1).

**Table 1.** Overview of the performance of carbon potentials for the relative energies of the 1812  $C_{60}$  isomers (in kcal mol<sup>-1</sup>). The reference values are obtained at the PW6B95-D3/Def2-QZVP level of theory.

Potential	$\mathbf{R}^{2,a}$	MAD <sup>b</sup>	MSD <sup>b</sup>	LND <sup>b</sup>
EDIP	0.725	127.6	-127.6	-217.6
ReaxFF-15	0.901	101.7	-101.7	-299.2
ABOP	0.931	96.5	-96.5	-279.6
AIREBO-M	0.794	95.9	-95.9	-334.6
AIREBO	0.796	95.7	-95.7	-332.3
ReaxFF-20	0.919	94.0	-94.0	-288.9
LCBOP-I	0.884	88.7	-88.7	-311.3
<b>REBO-II-S</b>	0.834	86.2	-86.2	-314.0
Tersoff	0.751	85.1	-85.1	-297.0
REBO-II	0.898	62.7	-62.7	-240.6
Tersoff-S	0.592	40.0	-38.2	-293.7
GAP-20	0.962	29.5	-29.5	-145.7

<sup>*a*</sup>Squared correlation coefficient between the force field and PW6B95-D3/Def2-QZVP isomerization energies. <sup>*b*</sup>MAD = mean absolute deviation, MSD = mean signed deviation, LND = largest negative deviation.

It is instructive to examine the squared correlation coefficients ( $R^2$ ) between the interatomic potential and PW6B95-D3/Def2-QZVP isomerization energies (Table 1). For Tersoff, Tersoff-S, AIREBO, AIREBO-M, and EDIP potentials, we obtain a low statistical correlation with the reference DFT isomerization energies, with  $R^2$  values < 0.8. The statistical

correlation is somewhat improved for the REBO-II-S potential with  $R^2 = 0.83$ , albeit it is still relatively poor. For five potentials (ReaxFF-15, ReaxFF-20, LCBOP-I, REBO-II, and ABOP) there is a reasonably high statistical correlation with the DFT isomerization energies with  $R^2 =$ 0.88 - 0.93. Remarkably, for the GAP-20 potential we obtain  $R^2 = 0.962$ . These results suggest that linear scaling of the isomerization energies may improve the accuracy of the latter carbon potentials.

Table 2 gives an overview of the performance of the scaled force-field isomerization energies. In all cases the scaling factor ( $\alpha$ ) has been optimized to minimize the MAD over the 1811 C<sub>60</sub> isomerization energies. We begin by making several general observations:

- $\Rightarrow$  The MADs are significantly improved by scaling the isomerization energies in most cases, they are reduced by 60–80% relative to the unscaled results.
- ⇒ With the exception of the EDIP potential, the scaled carbon potentials provide a balanced description of the isomerization energies, i.e., they no longer systematically underestimate the DFT reference values. In most cases the MSDs range between 0.1–1.6 kcal mol<sup>-1</sup> (in absolute value).
- $\Rightarrow$  With few exceptions (*vide infra*) the optimal scaling factors are on the order of ~2, i.e., on average, the potentials tend to underestimate the DFT isomerization energies by a factor of 2.

**Table 2.** Overview of the performance of carbon interatomic potentials for the relative energies of the 1812 C<sub>60</sub> isomers scaled by an empirical scaling factor ( $\alpha$ ) (in kcal mol<sup>-1</sup>). The reference values are PW6B95-D3/Def2-QZVP isomerization energies.

<b>Force Field</b>	$\alpha^{a}$	MAD <sup>b</sup>	MSD <sup>b</sup>	LND <sup>b</sup>	LPD <sup>b</sup>
EDIP	2.7034	51.4	-21.4	-183.5	387.6
Tersoff-S	1.2335	23.2	-2.8	-234.0	221.4
Tersoff	1.7963	19.1	-1.6	-96.2	141.8
AIREBO-M	2.0177	17.1	-0.3	-116.4	160.9
AIREBO	2.0150	17.0	-0.2	-112.3	161.0
ReaxFF-15	2.1182	15.8	-3.1	-73.9	124.4
ReaxFF-20	1.9440	15.2	-3.5	-75.8	104.7
<b>REBO-II-S</b>	1.8298	15.1	-0.2	-119.0	144.7
ABOP	2.0244	13.3	-1.0	-66.8	113.5
LCBOP-I	1.8781	12.3	0.1	-102.4	114.3
<b>REBO-II</b>	1.4897	12.3	-0.5	-89.6	113.4
GAP-20	1.1745	8.5	-1.5	-75.4	34.2

<sup>*a*</sup>Scaling factors optimized to minimize the MAD over the set of 1811  $C_{60}$  isomerization energies. <sup>*b*</sup>MAD = mean absolute deviation, MSD = mean signed deviation, LND = largest negative deviation, LPD = largest positive deviation.

For the EDIP potential we obtain a relatively high optimal scaling factor (2.7034) and  $MAD = 51.4 \text{ kcal mol}^{-1}$ . The Tersoff and Tersoff-S potentials show overall similar performance with MADs of 19.1 and 23.2 kcal mol<sup>-1</sup>, respectively. The AIREBO and AIREBO-M potentials attain essentially the same MADs (i.e., 17.0 and 17.1 kcal mol<sup>-1</sup>, respectively) with very similar optimal scaling factors. It is worth pointing out that the very small MSDs obtained for these force fields (i.e., -0.2 and -0.3 kcal mol<sup>-1</sup>, respectively) indicate that scaling the isomerization energies eliminates the systematic bias towards underestimation of the isomerization energies. Three carbon potentials (REBO-II-S, ReaxFF-15, and ReaxFF-20) are associated with similar MADs ranging between 15.1–15.8 kcal mol<sup>-1</sup>. Whereas the ABOP, REBO-II, and LCBOP-I potentials attain somewhat better performance with MADs ranging between 12.3–13.3 kcal mol<sup>-1</sup>.

The machine-learning GAP-20 potential is the only method that results in a MAD below 10 kcal mol<sup>-1</sup>, namely it attains a MAD of 8.5 kcal mol<sup>-1</sup>. In addition, the optimal scaling factor for the GAP-20 potential ( $\alpha = 1.1745$ ) is close to unity. This result, in addition to the high statistical correlation with the DFT isomerization energies of R<sup>2</sup> = 0.962, demonstrates that the GAP-20 potential is significantly less prone to underestimating the isomerization energies. We note, however, that the scaled GAP-20 procedure does not reach the accuracy of the best tight-binding method considered in Ref. 1. Namely, the DFTB-D3 method achieves an exceptionally low MAD of 5.3 kcal mol<sup>-1</sup> (see Ref. 1 for further details).

Finally, a comment is due on the computational cost of the considered carbon potentials. Figure S1 of the Supporting Information gives the relative central processing unit (CPU) times required by each of the carbon potentials to compute the energies of the entire set of 1812 C<sub>60</sub> isomers. As might be expected, the machine-learning GAP-20 potential has a computational cost which is noticeably higher than the classical interatomic potentials. For example, the computational cost of the GAP-20 potential is higher by a factor of ~2 relative to potentials such as LCBOP and ABOP, and by a factor of ~3 relative to potentials such as Tersoff-S and AIREBO.

*Performance of carbon potentials for energetically low-lying C*<sup>60</sup> *isomers.* In the previous section we have shown that the isomerization energies of the 1812 C<sup>60</sup> isomers represent a challenging test for carbon potentials, with only the GAP-20 potential attaining a MAD below the 10 kcal mol<sup>-1</sup> mark (MAD = 8.5 kcal mol<sup>-1</sup>) after scaling by an empirical scaling factor of  $\alpha = 1.1745$  (Table 2). This MAD translates to a mean-absolute relative deviation of 4.7%. However, since the C<sup>60</sup> isomerization energies span a very wide energetic window of 549.1 kcal mol<sup>-1</sup>, it is of interest to examine the performance of the potentials for the subset of 23 low-lying isomers associated with isomerization energies bellow 100 kcal mol<sup>-1</sup>. Table 3 gives

the error statistics for the scaled interatomic potentials, where in all cases the scaling factor ( $\alpha_{low}$ ) has been re-optimized to minimize the MAD over the energetically low-lying C<sub>60</sub> isomers. For this smaller subset of C<sub>60</sub> isomers, four potentials (REBO-II, LCBOP-I, ABOP, and GAP-20) attain MADs < 10 kcal mol<sup>-1</sup>, where the best performer is unsurprisingly GAP-20 with a MAD of 5.5 kcal mol<sup>-1</sup> (Table 3).

Force Field	$\alpha_{low}{}^a$	MAD <sup>b</sup>	MSD <sup>b</sup>	LND <sup>b</sup>	LPD <sup>b</sup>
EDIP	4.7039	24.8	-12.3	-74.6	44.7
ReaxFF-15	2.1354	13.4	-4.6	-29.0	14.9
Tersoff-S	1.0514	13.2	1.1	-25.6	27.6
Tersoff	1.5993	12.9	0.9	-26.5	21.7
AIREBO-M	1.8898	11.9	2.3	-22.3	20.7
AIREBO	1.8884	11.9	2.3	-22.2	20.7
ReaxFF-20	2.0838	11.4	-6.3	-31.8	11.7
REBO-II-S	1.7608	10.7	2.0	-22.0	17.7
REBO-II	1.4801	9.5	0.1	-23.4	14.3
LCBOP-I	1.8283	9.0	2.5	-19.4	16.0
ABOP	2.1125	7.9	-5.2	-31.8	7.4
GAP-20	1.2470	5.5	-0.1	-12.7	16.3

**Table 3.** Overview of the performance of carbon potentials for the relative energies of the 23 low-lying C<sub>60</sub> isomers scaled by an optimal empirical scaling factor ( $\alpha_{low}$ ) (in kcal mol<sup>-1</sup>). The reference values are PW6B95-D3/Def2-QZVP isomerization energies.

<sup>a</sup>Scaling factors optimized to minimize the MAD over the set of 23 energetically low-lying  $C_{60}$  isomers. <sup>b</sup>MAD = mean absolute deviation, MSD = mean signed deviation, LND = largest negative deviation, LPD = largest positive deviation.

Finally, it is of interest to compare the optimal scaling factors obtained for the entire set of 1812 isomers (Table 2) with those obtained for the subset of 23 low-lying isomers (Table 3). With the exception of EDIP, the scaling factors change by relatively small amounts. In particular, the two scaling factors differ (in absolute value) by 0.18–0.20 (Tersoff, Tersoff-S),

0.13–0.14 (AIREBO, AIREBO-M, ReaxFF-20), 0.05–0.09 (REBO-II-S, LCBOP-I, ABOP, GAP-20), and 0.01–0.02 (REBO-II, ReaxFF-15). These relatively small changes indicate the transferability of the optimal scaling factors between the two datasets of different sizes and energetic characteristics.

#### Conclusions

Fullerenes are key reference materials for the validation and parameterization of density functional and semiempirical molecular orbital theories. However, less attention has been given to the computationally more economical molecular mechanics methods. In this study, we evaluate the performance of 12 commonly used interatomic potentials which were specifically developed for carbon nanomaterials for a wide and diverse set of 1812 C60 isomers. The reference energies have been obtained at the PW6B95-D3/Def2-QZVP level of theory. Three important findings are that: (i) reoptimizing the C<sub>60</sub> isomers with the interatomic potentials leads to deterioration in performance relative to using the PBE-D3/Def2-TZVP geometries, (ii) all the carbon potentials tend to systematically underestimate the C<sub>60</sub> isomerization energies, and (iii) for several potentials (REBO-II, ReaxFF-15, ReaxFF-20, ABOP, and GAP-20) there is a high statistical correlation ( $R^2 = 0.90-0.96$ ) between the forcefield and DFT isomerization energies. Thus, linear scaling of the isomerization energies can significantly improve the accuracy of the carbon interatomic potentials. In particular, for the scaled GAP-20 potential we obtain a mean-absolute deviation of merely 8.5 kcal mol<sup>-1</sup>, which translates to mean-absolute relative deviation of merely 4.7%. Thus, this carbon potential offers a computationally efficient method for exploring the relative energies of fullerenes.

### Supplementary data

Mean-absolute deviations over the entire set of 1812 C<sub>60</sub> isomers for DFT and force-field optimized structures (Table S1); error statistics for unscaled and scaled force fields using force-field optimized structures (Tables S2–S4); absolute energies for the 1812 C<sub>60</sub> isomers for all the considered force fields using DFT and force-field optimized structures (Tables S5 and S6); computational cost of the considered carbon potentials (Figure S1).

# Acknowledgments

We gratefully acknowledge the generous allocation of computing time from the National Computational Infrastructure (NCI) National Facility, and system administration support provided by the Faculty of Science at UWA to the Linux cluster of the Karton group. AK is the recipient of an Australian Research Council (ARC) Future Fellowship (Project No. FT170100373).

# References

<sup>1</sup> R. Sure, A. Hansen, P. Schwerdtfeger, S. Grimme, Comprehensive theoretical study of all 1812 C<sub>60</sub> isomers. Phys. Chem. Chem. Phys. 19 (2017) 14296.

<sup>2</sup> P. Schwerdtfeger, L. N. Wirz, J. Avery, The topology of fullerenes, WIREs Comput. Mol. Sci. 5 (2014) 96.

<sup>3</sup> S. L. Waite, A. Karton, B. Chan, A. J. Page, Thermochemical Stabilities of Giant Fullerenes using Density Functional Tight Binding Theory with Isodesmic-Type Reactions. J. Comput. Chem. 42 (2021) 222. <sup>4</sup> B. Chan, Fullerene Thermochemical Stability: Accurate Heats of Formation for Small Fullerenes, the Importance of Structural Deformation on Reactivity, and the Special Stability of C<sub>60</sub>, Phys. Chem. A 124 (2020) 6688.

<sup>5</sup> A. Karton, S. L. Waite, A. J. Page. Performance of DFT for C<sub>60</sub> Isomerization Energies: A Noticeable Exception to Jacob's Ladder. J. Phys. Chem. A 123 (2019) 257.

<sup>6</sup> B. Chan, Y. Kawashima, W. Dawson, M. Katouda, T. Nakajima, K. Hirao, A Simple Model for Relative Energies of All Fullerenes Reveals the Interplay between Intrinsic Resonance and Structural Deformation Effects in Medium-Sized Fullerenes, J. Chem. Theory Comput. 15, (2019) 1255.

<sup>7</sup> M. A. Hashmi, M. Lein, Carbon Nano-onions as Photosensitizers: Stacking-Induced Red-Shift, J. Phys. Chem. C 122 (2018) 2422.

<sup>8</sup> A. Karton, B. Chan, K. Raghavachari, L. Radom. Evaluation of the heats of formation of corannulene and C<sub>60</sub> by means of high-level theoretical procedures. J. Phys. Chem. A, 117 (2013) 1834.

<sup>9</sup> A. Aghajamali, Atomistic simulations of diamond: Implantation, annealing, deformation and relaxation, Ph.D. thesis, Curtin University (2020). Available at: http://hdl.handle.net/20.500.11937/82668

<sup>10</sup> C. de Tomas, A. Aghajamali, J. L. Jones, D. J. Lim, M. J. López, I. Suarez-Martinez, N. A. Marks, Transferability in interatomic potentials for carbon, Carbon 155 (2019) 624.

<sup>11</sup> C. de Tomas, I. Suarez-Martinez, N. A. Marks, Graphitization of amorphous carbons: A comparative study of interatomic potentials, Carbon 109 (2016) 681.

<sup>12</sup> L. N. Wirz, R. Tonner, A. Hermann, R. Sure, P. Schwerdtfeger, From small fullerenes to the graphene limit: A harmonic force-field method for fullerenes and a comparison to density functional calculations for Goldberg–Coxeter fullerenes up to C<sub>980</sub>, 37 (2016) 10.

<sup>13</sup> N. A. Marks, Amorphous carbon and related materials, in: Computer-Based Modeling of Novel Carbon Systems and Their Properties, Springer, 2010, pp. 129-169.

<sup>14</sup> O. T. Unke, S. Chmiela, H. E. Sauceda, M. Gastegger, I. Poltavsky, K. T. Schütt, A. Tkatchenko, K.-R. Müller, Machine Learning Force Fields, Chem. Rev. 2021, available online: https://doi.org/10.1021/acs.chemrev.0c01111.

<sup>15</sup> Q. Liua, L. Li, Y.-R. Jeng, G. Zhang, C. Shuai, X. Zhu, Effect of interatomic potentials on modeling the nanostructure of amorphous carbon by liquid quenching method, Comput. Mater. Sci. 184 (2020) 109939.

<sup>16</sup> S. Best, J. B. Wasley, C. de Tomas, A. Aghajamali, I. Suarez-Martinez, N. A. Marks, Evidence for Glass Behavior in Amorphous Carbon, C 6 (2020) 50.

<sup>17</sup> R. Jana, D. Savio, V. L. Deringer, L. Pastewka, Structural and elastic properties of amorphous carbon from simulated quenching at low rates, Modelling Simul. Mater. Sci. Eng. 27 (2019) 085009.

<sup>18</sup> F. Gayk, J. Ehrens, T. Heitmann, P. Vorndamme, A. Mrugalla, J. Schnack, Young's moduli of carbon materials investigated by various classical molecular dynamics schemes, Physica E Low Dimens. Syst. Nanostruct. 99 (2018) 215.

<sup>19</sup> Xiaowei Li, Aiying Wang, K.-R. Lee, Comparison of empirical potentials for calculating structural properties of amorphous carbon films by molecular dynamics simulation, Comput. Mater. Sci. 151 (2018) 246.

<sup>20</sup> G. M. Galiullina, N. D. Orekhov, V. V. Stegailov, Nucleation of carbon nanostructures: Molecular dynamics with reactive potentials, J. Phys. Conf. Ser. 774 (2016) 012033.

<sup>21</sup> C. D. Latham, A. J. McKenna, T. P. Trevethan, M. I. Heggie, M. J. Rayson, P. R. Briddon, On the validity of empirical potentials for simulating radiation damage in graphite: a benchmark, J. Phys.: Condens. Matter 27 (2015) 316301.

<sup>22</sup> L. Li, M. Xu,W. Song, A. Ovcharenko, G. Zhang, D. Jia, The effect of empirical potential functions on modeling of amorphous carbon using molecular dynamics method, Appl. Surf. Sci. 286 (2013) 287.

<sup>23</sup> J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple,
Phys. Rev. Lett. 77 (1996) 3865.

<sup>24</sup> Y. Zhao, D. G. Truhlar, Design of Density Functionals That Are Broadly Accurate for Thermochemistry, Thermochemical Kinetics, and Nonbonded Interactions, J. Phys. Chem. A 109 (2005) 5656.

<sup>25</sup> F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, Phys. Chem. Chem. Phys. 7 (2005) 3297.

<sup>26</sup> C. Riplinger, B. Sandhoefer, A. Hansen, F. Neese, Natural triple excitations in local coupled cluster calculations with pair natural orbitals, J. Chem. Phys. 139 (2013) 134101.

<sup>27</sup> H. Kruse, A. Mladek, K. Gkionis, A. Hansen, S. Grimme, J. Sponer, Quantum Chemical Benchmark Study on 46 RNA Backbone Families Using a Dinucleotide Unit, J. Chem. Theory Comput. 11 (2015) 4972. <sup>28</sup> J. Tersoff, Empirical Interatomic Potential for Carbon, with Applications to Amorphous Carbon, Phys. Rev. Lett. 61 (1988) 2879.

<sup>29</sup> L. Pastewka, A. Klemenz, P. Gumbsch, M. Moseler, Screened empirical bond-order potentials for Si-C, Phys. Rev. B 87 (2013) 205410.

<sup>30</sup> N. A. Marks, Generalizing the environment-dependent interaction potential for carbon, Phys.
Rev. B 63 (2000) 035401.

<sup>31</sup> D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, S. B. Sinnott, A secondgeneration reactive empirical bond order (REBO) potential energy expression for hydrocarbons, J. Condens. Matter Phys. 14 (2002) 783.

<sup>32</sup> L. Pastewka, P. Pou, R. Pérez, P. Gumbsch, M. Moseler, Describing bond-breaking processes by reactive potentials: Importance of an environment-dependent interaction range, Phys. Rev. B 78 (2008) 161402(R).

<sup>33</sup> S. J. Stuart, A. B. Tutein, J. A. Harrison, A reactive potential for hydrocarbons with intermolecular interactions, J. Chem. Phys. 112 (2000) 6472.

<sup>34</sup> T. C. O'Connor, J. Andzelm, M. O. Robbins, AIREBO-M: A reactive model for hydrocarbons at extreme pressures, J. Chem. Phys. 142 (2015) 024903.

<sup>35</sup> J. H. Los, A. Fasolino, Intrinsic long-range bond-order potential for carbon: Performance in Monte Carlo simulations of graphitization, Phys. Rev. B 68 (2003) 024107.

<sup>36</sup> D. G. Pettifor, I. I. Oleinik, Analytic bond-order potentials beyond Tersoff-Brenner. I. Theory, Phys. Rev. B 59 (13) (1999)8487.

<sup>37</sup> X. W. Zhou, D. K. Ward, M. E. Foster, An analytical bond-order potential for carbon, J. Comput. Chem. 36 (2015) 1719.

<sup>38</sup> A. C. T. van Duin, S. Dasgupta, F. Lorant, W. A. Goddard. ReaxFF: a reactive force field for hydrocarbons. J. Phys. Chem. A, 105 (2001) 9396.

<sup>39</sup> S. G. Srinivasan, A. C. T. van Duin, P. Ganesh, Development of a ReaxFF Potential for Carbon Condensed Phases and Its Application to the Thermal Fragmentation of a Large Fullerene, J. Phys. Chem. A 119 (2015) 571.

<sup>40</sup> C. Ashraf, A. Jain, Y. Xuan, A. C. T. van Duin, ReaxFF based molecular dynamics simulations of ignition front propagation in hydrocarbon/oxygen mixtures under high temperature and pressure conditions, Phys. Chem. Chem. Phys.19 (2017) 5004.

<sup>41</sup> B. Damirchi, M. Radue, K. Kanhaiya, H. Heinz, G. M. Odegard, A. C. T. van Duin, ReaxFF Reactive Force Field Study of Polymerization of a Polymer Matrix in a Carbon Nanotube-Composite System, J. Phys. Chem. C 124 (2020) 20488.

<sup>42</sup> P. Rowe, V. L. Deringer, P. Gasparotto, G. Csányi, A. Michaelides, An accurate and transferable machine learning potential for carbon, J. Chem. Phys. 153 (2020) 034702.

<sup>43</sup> S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, J. Comp. Phys.,
117, 1 (1995).

<sup>44</sup> LAMMPS version 10 Mar 2021 was used, see also the LAMMPS website: http://lammps.sandia.gov.