The Journal of Physical Chemistry Letters

Letter

Cite This: J. Phys. Chem. Lett. 2018, 9, 359−363

pubs.acs.org/JPCL

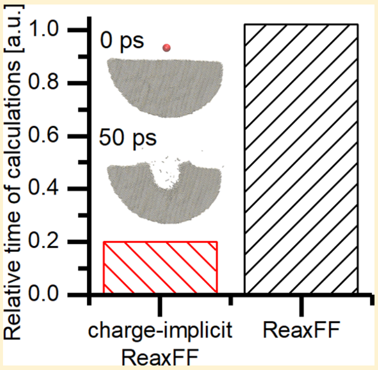
Development of a Charge-Implicit ReaxFF Potential for Hydrocarbon Systems

Michał Kański,*,† Dawid Maciążek,† Zbigniew Postawa,† Chowdhury M. Ashraf,‡ Adri C. T. van Duin,‡ and Barbara J. Garrison*,§

†Smoluchowski Institute of Physics, Jagiellonian University, ul. Lojasiewicza 11, 30-348 Krakow, Poland
‡Department of Mechanical and Nuclear Engineering, Penn State University, University Park, Pennsylvania 16802, United States
§Department of Chemistry, Penn State University, 104 Chemistry Building, University Park, Pennsylvania 16802, United States

Supporting Information

ABSTRACT: Molecular dynamics (MD) simulations continue to make important contributions to understanding chemical and physical processes. Concomitant with the growth of MD simulations is the need to have interaction potentials that both represent the chemistry of the system and are computationally efficient. We propose a modification to the ReaxFF potential for carbon and hydrogen that eliminates the time-consuming charge equilibration, eliminates the acknowledged flaws of the electronegativity equalization method, includes an expanded training set for condensed phases, has a repulsive wall for simulations of energetic particle bombardment, and is compatible with the LAMMPS code. This charge-implicit ReaxFF potential is five times faster than the conventional ReaxFF potential for a simulation of keV particle bombardment with a sample size of over 800 000 atoms.



Molecular dynamics (MD) computer simulations are widely used to gain microscopic insights into processes as either a complement to or a substitute for experimental investigations. The key component of the MD methodology is an interatomic potential (or force field) that describes interactions among atoms or other particles in the system under investigation. Consequently, there have been numerous studies aimed at developing interatomic potentials. The main goals have been to make the potentials more accurate at describing the interactions or chemistry of interest and to increase the number of elements that can be modeled. More accuracy has inevitably led to more computationally expensive interatomic potentials. An example is the ReaxFF potential that has been developed for about 50 elements.[1] The goal of chemical accuracy and thus the versatility of the potential is due in part to a Coulombic interaction term with fluctuating charges. The charge equilibration is computationally expensive and must be evaluated at every integration step. In addition to the high computational cost, the procedure for the charge determination adopted in the noncommercially available versions of ReaxFF is based on the electronegativity equalization method (EEM).[2] It has been reported that the EEM does not work properly for systems in which molecules undergo significant fragmentation because the EEM performs charge equilibration for the entire system, rather than for individual molecules or fragments.[3,4] For example, in simulations of keV particle impacts on solids, it was observed that charged particles are ejected from the sample.[4] The emission of charge particles is an unphysical behavior as ReaxFF is not designed to model ionization, and all fragments should remain neutral. In order to solve these issues, a different charge equilibration procedure based on the atom-condensed Kohn−Sham density functional theory approximated to second order (ACKS2) approach has been proposed recently.[5] Although others are starting to use the ACKS2 charge equilibration algorithm to eliminate the problems associated with the EEM method,[6] charge equilibration remains a time-consuming quantity for each integration step.

There are multiple objectives in MD simulations with corresponding differences in system size, length of time of the chemical and physical processes to be simulated, and chemical accuracy required of the interaction potential. For example, our simulations of keV particle bombardment require millions of atoms to be modeled for tens of ps. In this case, to accurately describe all of the reactions including charge transfer is beyond the scope of classical mechanics, yet MD simulations have been extremely useful in interpreting experimental data with empirical potentials that help delineate where and when chemical reactions occur[7,8] and, in some cases, the nature of the chemical reactions.[9] There is thus a pressing need to explore interaction potentials that contain reasonable chemistry and are more computationally efficient. In order to achieve this goal, we have refit the ReaxFF hydrocarbon (CH) potential (ReaxFF-2008),[10] omitting the electrostatic term between pairs

Received: November 28, 2017
Accepted: January 1, 2018
Published: January 1, 2018

of atoms. The ReaxFF potential, after all, has hundreds of parameters to compensate for the lack of explicit charges, and the charge only appears in one electrostatic term. Moreover, the elements of C and H have similar electronegativity; therefore, one would not expect much charge transfer. The charge-implicit ReaxFF (ci-ReaxFF) fits the training set data at the same level as ReaxFF-2008 using the metric of agreement in the fitting code[11] and is 2−5 times faster for MD calculations of 13 000−900 000 atoms.

Development of the ci-ReaxFF requires a complete refitting of the parameters for each pair of elements; thus, we include two additional modifications that are needed for our own simulations. First, we are interested in condensed phases, and although the basic ReaxFF functional form does contain a long-range term, there has not been an emphasis on using condensed phases in the training set except for a potential developed by Liu et al.,[12] which is referred to as ReaxFF-lg. Second, we are interested in high-energy keV collisions[7] and need a potential that extends to shorter distances and higher energies than the basic ReaxFF potential. The potential development has been done to be consistent with the LAMMPS implementation of ReaxFF,[13] and resulting input potential files with the usage example are placed in the Supporting Information.

The overall strategy is to augment the ReaxFF-2008 training set with energies and geometries of condensed phases and short-ranged energies and forces from the Ziegler−Biersack−Littmark (ZBL) potential,[14] which is widely used for modeling high-energy collisions. The ZBL energy values are included with weights inversely proportional to the energy. The ReaxFF potential parameters are refit as described below. Finally, the short-ranged repulsive wall is corrected by a tabulated functional form. Before discussing the fitting procedure, the issue of cutoff distance is addressed. The computational efficiency of a potential is linked with its cutoff distance as the number of interactions between atoms rises with the third power of the cutoff distance. The ReaxFF formalism utilizes three distinct cutoff distances,[10] one for chemical bonds, one for the hydrogen bond term, and one for nonbonded interactions including both electrostatic and van der Waals interactions. The values are virtually identical for all existing ReaxFF parametrizations, that is, 5, 7.5, and 10 Å, for the three interactions, respectively.[10,12,15] Even though the same cutoff distance is used for the electrostatic and van der Waals interactions, one would expect that the cutoff distance for the van der Waals term should be shorter than that for the electrostatic term, which is not present in the ci-ReaxFF potential. The following procedure is employed in order to choose the new cutoff distance. A sample consisting of 63 β-carotene molecules is equilibrated at 300 K and 1 atm in an *NPT* ensemble during an 83 ps simulation. The ReaxFF-lg potential[12] is used because it allows one to extract explicitly the long-ranged van der Waals energies. When the van der Waals interaction energies of all atoms between 7 and 10 Å are set to zero, the energy change is 1×10^{-2} kcal/mol (1%) and 8×10^{-4} kcal/mol (0.2%) for C and H atoms, respectively. We consider this a negligible change and thus will use a cutoff distance of 7 Å for the ci-ReaxFF potential. This reduction in cutoff distance eliminates 2/3 of the neighbors, a substantial reduction in computational effort.

The original training set used for fitting the CH portion of ReaxFF developed in 2008 (ReaxFF-2008) is comprised of about 700 reference values.[10] For the development of the ci-ReaxFF, we have included the experimental values of densities of molecular systems of ethane, benzene, cyclohexane, β-carotene, polyethylene, and polystyrene and the interlayer spacing of graphite, as given in Table 1, and the heats of vaporization of these molecules (excluding the polymers) and the interlayer cohesive energy of graphite, as given in Table 2.

Table 1. Geometrical Quantities, Densities of Molecular Systems in g/cm^3, and Interatomic Spacing in Graphite in Å[a]

system	expt	ReaxFF-2008	ci-ReaxFF
ethane[16]	0.546	0.72	0.71
benzene[16]	0.877	1.19	0.93
cyclohexane[16]	0.774	0.86	0.88
β-carotene[17]	1.00	1.06	1.06
polyethylene[17]	0.92−0.97	0.94	1.07
polystyrene[18]	1.04−1.065	1.27	1.19
graphite[17]	3.35	3.19	3.36

[a] Experimental temperatures are 184 K for ethane, 293 K for benzene, and 298 K for the next five systems.

Table 2. Long-Range Energetics, Heats of Vaporization of Molecular Solids, and Interlayer Cohesive Energy in Graphite in kcal/mol[a]

system	expt	ReaxFF-2008	ci-ReaxFF
ethane[16]	3.51	5.38	4.08
benzene[16]	7.89	12.87	6.30
cyclohexane[16]	7.89	9.07	7.93
graphite[19]	1.43	1.77	1.60

[a] The experimental temperatures are 184, 293, 298, and 298 K, respectively.

These values were added to the training set to improve long-range, dispersive predictions of the new potential. All potential parameters were refit to comply with the extended training set.

The fitting procedure is as follows. In the first step, the parameters in the ReaxFF potential connected to bonding interactions were optimized using a successive one-parameter search technique, as described in ref 11 for the expanded training set. In general, our aim was to reproduce heats of formation to within 4.0 kcal/mol, bond lengths to within 0.01 Å, and bond angles to within 2° of their literature values, as with previous fits of the ReaxFF potential. Subsequently, the densities and heats of vaporization were computed with the procedure described in the Supporting Information and compared with the experimental values. On the basis of the difference between the reference and calculated values, the parameters of the nonbonding interactions were adjusted and the parameters of the bonding interactions were refit. The procedure was repeated until the deviation from reference values of densities and heats of vaporization was below 15% for the majority of reference values. At this point, calculations of the densities and heats of vaporization were performed with an extended simulation time. If the values were in desired agreement with the reference values, the fitting was finished. Otherwise, the parameters of the nonbonding interactions were further adjusted.

The geometrical quantities predicted by the ReaxFF-2008 and ci-ReaxFF potentials are given in Table 1. On average, the values for ReaxFF-2008 are 16% higher than the experimental

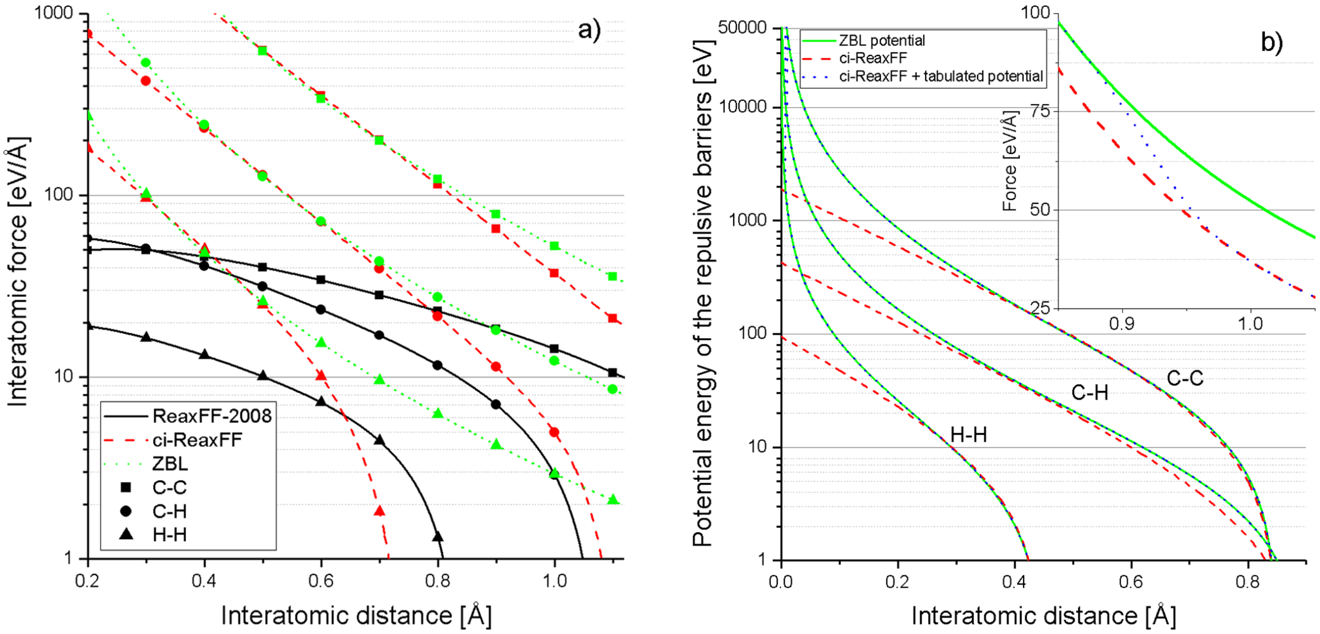


Figure 1. (a) Comparison of carbon−carbon (squares), carbon−hydrogen (circles), and hydrogen−hydrogen (triangles) close-range forces predicted by ReaxFF-2008 (black continuous lines) and the charge-implicit ReaxFF (red dashed lines) to the reference data (green dotted lines). (b) Potential energy of the close-range interactions predicted by the ZBL potential (green continuous line), the ci-ReaxFF (red dashed line), and the ci-ReaxFF with the additional tabulated potential (blue dotted line) relative to energy at the end of the splining region, R_1, as given in the text. The inset shows the force of the interaction in the splining region for C−C interactions.

values and the values for the ci-ReaxFF differ by 12% and are mostly higher. The calculated values of long-range energetics are given in Table 2. On average, the values for ReaxFF-2008 are 39% higher than the experimental values and the values for the ci-ReaxFF differ by 12%. Because the ci-ReaxFF has been fit to condensed phase energetics and geometries, it fits the experimental data better. The parameters for the ci-ReaxFF potential are given in the Supporting Information.

The last step of the potential development involves the short-ranged repulsive interactions. The ReaxFF formalism does include a term that can be used to describe the potential energy of the short-range interactions, namely, E_{core},[11] which is given by

$$E_{\text{core}} = e_{\text{core}} \cdot \exp\left[a_{\text{core}} \cdot \left(1 - \frac{r_{ij}}{r_{\text{core}}}\right)\right] \tag{1}$$

where r_{ij} is a distance between pairs of atoms, and e_{core}, a_{core}, and r_{core} are parameters of the function. The functional form of this term, however, is different from the functional form of the ZBL potential that contains a screened Coulomb interaction.[14] It is not surprising, therefore, that satisfactory agreement between the ci-ReaxFF and the ZBL potential can be obtained only in a relatively narrow range of distances, as shown in Figure 1a. To extend this range to shorter distances, a tabulated potential was created using the following formula

$$F[r_{ij}] = \begin{cases} F_{\text{ZBL}}[r_{ij}] - F_{\text{ci-ReaxFF}}[r_{ij}] & \text{for } r_{ij} < R_1 \\ T[F_{\text{ZBL}}[r_{ij}] - F_{\text{ci-ReaxFF}}[r_{ij}]] & \text{for } R_1 \le r_{ij} \le R_2 \\ 0 & \text{for } r_{ij} > R_2 \end{cases} \tag{2}$$

where $F[r_{ij}]$ is a tabulated force, $F_{\text{ZBL}}[r_{ij}]$ is the force obtained from the ZBL force field, $F_{\text{ci-ReaxFF}}[r_{ij}]$ is the force calculated from the ci-ReaxFF, and R_1 and R_2 are interatomic distances defining the splining region. The values of (R_1, R_2) in Å are (0.85, 1.00), (0.90, 1.10), and (0.45, 0.60) for C−C, C−H, and H−H, respectively. The potential energy of the tabulated force field was calculated by numerical integration of the force. The splining function, $T[x]$, was adopted from the ReaxFF formalism[10] and is defined as follows

$$T[F[r_{ij}]] = F[r_{ij}] \cdot \left[20\frac{(r_{ij} - R_1)^7}{(R_2 - R_1)^7} - 70\frac{(r_{ij} - R_1)^6}{(R_2 - R_1)^6} + 84\frac{(r_{ij} - R_1)^5}{(R_2 - R_1)^5} - 35\frac{(r_{ij} - R_1)^4}{(R_2 - R_1)^4} + 1\right] \tag{3}$$

As shown in Figure 1b, the addition of the tabulated potential increases the range of agreement with the ZBL up to an interatomic distance equal to about 0.01 Å. The tabulated potential file in a LAMMPS format is given in the Supporting Information.

The same test systems as those in the original paper on the hydrocarbon ReaxFF potential[20] were used to verify the accuracy of the new parametrization. These plots are given in the Supporting Information. The fitting code uses a parameter to quantify the quality of the fit, which is essentially a weighted sum of squares of the energy differences between the predicted energy and the training set energy. This parameter is 0.6% smaller for ci-ReaxFF than that for ReaxFF-2008; thus, we feel that the new charge-implicit formulation represents the ReaxFF-2008 values. In order to investigate reactions taking place in a more energetic environment, calculations of the activation energy and pre-exponential factor of JP-10 (exotricyclo[5.2.1.0]decane) and toluene pyrolysis were performed. The temperatures used for the simulations are higher than the experimental ones because of the high energy barrier of the pyrolysis. There is a difference of 12 kcal/mol in

Table 3. CPU Times in Minutes for Various Systems Using the ci-ReaxFF and ReaxFF-lg Potentials

system	number of particles	number of time steps	number of cores	ReaxFF-lg	ci-ReaxFF	ratio lg/ci
polystyrene	13 000	500 000	8	1660	750	2.2
C_{60}/graphite	910 000	25 000	36	1325	461	2.9
C_{60}/octatetraene	822 000	25 000	40	1296	250	5.2

the activation energy of JP-10 pyrolysis between ci-ReaxFF and ReaxFF-2008. This difference is not present in the case of toluene, however. A detailed comparison of the results is given in the Supporting Information. The comparison of the ci-ReaxFF to the ReaxFF-2008 potential looks favorable; thus, the important factor becomes the computational efficiency.

Three MD test simulations were performed to compare the computational efficiency of the ci-ReaxFF potential. In particular, we wanted to test the ci-ReaxFF potential for energetic collisions. As the comparison potential we used the ReaxFF-lg potential,[12] which is the only previous ReaxFF potential to have had a short-ranged interaction incorporated in it. ReaxFF-lg contains one more term for long-ranged interactions than ReaxFF-2008 but the same cutoff distances as ReaxFF-2008; thus, we expect the speeds of ReaxFF-2008 and ReaxFF-lg to be similar. Details of the simulations are given in the Supporting Information. The first simulation consists of polystyrene chains equilibrated in an *NVT* ensemble for 500 000 time steps. The second and third simulations are C_{60} bombardment of graphite and octatetraene evaluated for 25 000 time steps. The CPU times are given in Table 3. The speed-up is a factor of 2−5 depending on the system. Finally, the C_{60}/octatetraene simulation was evaluated to 50 ps and the final crater examined, as shown in Figure 2. The crater is similar to ones formed using the same beam/substrate conditions with other CH potentials[4] including ReaxFF-lg with a modified method for the EEM implementation. The calculated yield with the ci-ReaxFF and ReaxFF-lg potentials is 140 nm^3.

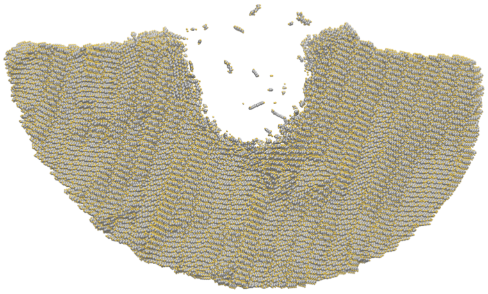


Figure 2. Cross section of thickness 40 Å of the octatetraene sample bombarded by a 15 keV C_{60} projectile at normal incidence 50 ps after the impact. The interatomic potential used was ci-ReaxFF. Carbon and hydrogen atoms are represented by silver and yellow balls, respectively.

The charge-implicit ReaxFF was developed in order to increase computational efficiency of the ReaxFF potential and to resolve problems associated with the EEM charge equilibration procedure. The electrostatic term was eliminated from the potential, and the effects of charge interactions were incorporated into the other terms by refitting the parameters. The lack of explicit electrostatic interactions allowed for reduction of the nonbonded cutoff distance from 10 to 7 Å. The new ci-ReaxFF fits the reference data to within 0.6% of ReaxFF-2008 and is 2−5 times faster. In addition, ci-ReaxFF was fit to condensed phase energetics and geometries, and a repulsive wall was added for energetic collisions. We believe that the ci-ReaxFF potential should be applicable to any system investigated by the ReaxFF-2008 potential with only C and H atoms. The advantage of the ci-ReaxFF potential is the increased computational efficiency, the better fit to condensed phase systems, and the repulsive wall for energetic collisions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b03155.

Potential file in a native ReaxFF format (TXT)
File with tabulated corrections for a short-range interaction, written in the LAMMPS format (TXT)
Example of usage of the charge-implicit ReaxFF with tabulated correction in LAMMPS (version 1SEP2017) (PDF)
Procedures for obtaining heats of vaporization, densities of materials, and the interlayer cohesive energy per atom of graphite, list of parameters of the force field, comparison of bond dissociation curves predicted by ci-ReaxFF to ReaxFF-2008 and DFT calculations, and detailed results of pyrolysis simulations and details of test simulations used to measure computational efficiency of the ci-ReaxFF potential (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: michal.kanski@uj.edu.pl (M.K.).
*E-mail: bjg@psu.edu. Phone: 1-814-863-2103 (B.J.G.).

ORCID

Barbara J. Garrison: 0000-0002-7053-5284

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was partially supported by the National Institutes of Health (Grant 5R01GM113746-22), the Polish National Science Center, Grants 2015/19/B/ST4/01892 and 2016/23/N/ST4/01013, a stipend to M.K. funded by Krakowskie Konsorcjum Naukowe im. Mariana Smoluchowskiego “Materia−Energia−Przyszłość” as a part of the KNOW endowment, and AFOSR Grants FA9550-14-1-0355 and FA9550-17-1-0173.

■ REFERENCES

(1) Senftle, T. P.; Hong, S.; Islam, M. M.; Kylasa, S. B.; Zheng, Y.; Shin, Y. K.; Junkermeier, C.; Engel-Herbert, R.; Janik, M. J.; Aktulga, H. M.; et al. The ReaxFF Reactive Force-Field: Development, Applications and Future Directions. *Nature* **2016**, *2*, 15011.

(2) Mortier, W. J.; Ghosh, S. K.; Shankar, S. Electronegativity Equalization Method for the Calculation of Atomic Charges in Molecules. *J. Am. Chem. Soc.* **1986**, *108*, 4315−4320.

(3) Chen, J. H.; Martinez, T. J. Qtpie: Charge Transfer with Polarization Current Equalization. A Fluctuating Charge Model with Correct Asymptotics. *Chem. Phys. Lett.* **2007**, *438*, 315−320.

(4) Kanski, M.; Maciazek, D.; Golunski, M.; Postawa, Z. Sputtering of Octatetraene by 15 keV C_{60} Projectiles: Comparison of Reactive Interatomic Potentials. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2017**, *393*, 29−33.

(5) Verstraelen, T.; Ayers, P. W.; van Speybroeck, V.; Waroquier, M. Acks2: Atom-Condensed Kohn-Sham DFT Approximated to Second Order. *J. Chem. Phys.* **2013**, *138*, 074108.

(6) Islam, M. M.; Kolesov, G.; Verstraelen, T.; Kaxiras, E.; van Duin, A. C. T. Ereaxff: A Pseudoclassical Treatment of Explicit Electrons within Reactive Force Field Simulations. *J. Chem. Theory Comput.* **2016**, *12*, 3463−3472.

(7) Garrison, B. J.; Postawa, Z. Computational View of Surface Based Organic Mass Spectrometry. *Mass Spectrom. Rev.* **2008**, *27*, 289−315 and references therein..

(8) Garrison, B. J.; Postawa, Z. Molecular Dynamics Simulations, the Theoretical Partner to Dynamic Cluster SIMS Experiments. In *ToF-SIMS − Surface Analysis by Mass Spectrometry*, 2nd ed.; Vickerman, J. C., Briggs, D., Eds.; IMP & SurfaceSpectra Ltd: Chichester, Manchester, U.K., 2013; pp 151−192, and references therein.

(9) Kanski, M.; Garrison, B. J.; Postawa, Z. Effect of Oxygen Chemistry in Sputtering of Polymers. *J. Phys. Chem. Lett.* **2016**, *7*, 1559−1562.

(10) Chenoweth, K.; van Duin, A. C. T.; Goddard, W. A. ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation. *J. Phys. Chem. A* **2008**, *112*, 1040−1053.

(11) van Duin, A. C. T.; Baas, J. M. A.; Vandegraaf, B. Delft Molecular Mechanics - a New Approach to Hydrocarbon Force-Fields - Inclusion of a Geometry-Dependent Charge Calculation. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2881−2895.

(12) Liu, L. C.; Liu, Y.; Zybin, S. V.; Sun, H.; Goddard, W. A. ReaxFF-Lg: Correction of the ReaxFF Reactive Force Field for London Dispersion, with Applications to the Equations of State for Energetic Materials. *J. Phys. Chem. A* **2011**, *115*, 11016−11022.

(13) Aktulga, H. M.; Fogarty, J. C.; Pandit, S. A.; Grama, A. Y. Parallel Reactive Molecular Dynamics: Numerical Methods and Algorithmic Techniques. *Parallel Computing* **2012**, *38*, 245−259.

(14) Ziegler, J. F.; Biersack, J. P.; Littmark, U. The Stopping Power and Ranges of Ions in Matter. In *The Stopping and Range of Ions in Solids*; Ziegler, J. F., Ed.; Pergamon: New York, 1985; Vol. *1*.

(15) Jarvi, T. T.; van Duin, A. C. T.; Nordlund, K.; Goddard, W. A. Development of Interatomic ReaxFF Potentials for Au-S-C-H Systems. *J. Phys. Chem. A* **2011**, *115*, 10315−10322.

(16) Wang, J.; Hou, T. Application of Molecular Dynamics Simulations in Molecular Property Prediction. 1. Density and Heat of Vaporization. *J. Chem. Theory Comput.* **2011**, *7*, 2151−2165.

(17) Haynes, W. M. *CRC Handbook of Chemistry and Physics*, 97th ed.; CRC Press, 2016.

(18) Mark, J. E. *Polymer Data Handbook*; Oxford University Press, 1999.

(19) Zacharia, R.; Ulbricht, H.; Hertel, T. Interlayer Cohesive Energy of Graphite from Thermal Desorption of Polyaromatic Hydrocarbons. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *69*, 155406.

(20) van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A. ReaxFF: A Reactive Force Field for Hydrocarbons. *J. Phys. Chem. A* **2001**, *105*, 9396−9409.

DOI: 10.1021/acs.jpclett.7b03155
J. Phys. Chem. Lett. 2018, 9, 359−363