

# Parametric Study of ReaxFF Simulation Parameters for Molecular Dynamics Modeling of Reactive Carbon Gases

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**S** Supporting Information

**ABSTRACT:** The development of innovative carbon-based materials can be greatly facilitated by molecular modeling techniques. Although the Reax Force Field (ReaxFF) can be used to simulate the chemical behavior of carbon-based systems, the simulation settings required for accurate predictions have not been fully explored. Using the ReaxFF, molecular dynamics (MD) simulations are used to simulate the chemical behavior of pure carbon and hydrocarbon reactive gases that are involved in the formation of carbon structures such as graphite, buckyballs, amorphous carbon, and carbon nanotubes. It is determined that the maximum simulation time step that can be used in MD simulations with the ReaxFF is dependent on the simulated temperature and selected parameter set, as are the predicted reaction rates. It is also determined that different carbon-based reactive gases react at different rates, and that the predicted equilibrium structures are generally the same for the different ReaxFF parameter sets, except in the case of the predicted formation of large graphitic structures with the Chenoweth parameter set under specific conditions.

## 1. INTRODUCTION

Carbon-based materials are ideal for many structural aerospace components, because of their high specific strength and high specific stiffness, relative to traditional aerospace metallic materials. Reactive carbon-based gases are commonly used in the synthesis of carbon-based nanostructured materials. Various reactive gas processes occur in the production of carbon-based material constituents such as nanotubes, amorphous carbon films, and even soot particles formed from combustion. Electron beam deposition,<sup>1</sup> chemical vapor deposition,<sup>2,3</sup> pulsed arc discharge deposition,<sup>4</sup> plasma deposition,<sup>5–8</sup> pulsed laser deposition,<sup>1,9</sup> laser ablation, combustion,<sup>10,11</sup> and ion beam irradiation<sup>12</sup> are all processes that are used in the manufacture of carbon-based materials where the source of carbon is a reactive carbon-based gas. Because of the wide range of processing methods and conditions that can be used to fabricate carbon-based materials, their development can be time-consuming and expensive.

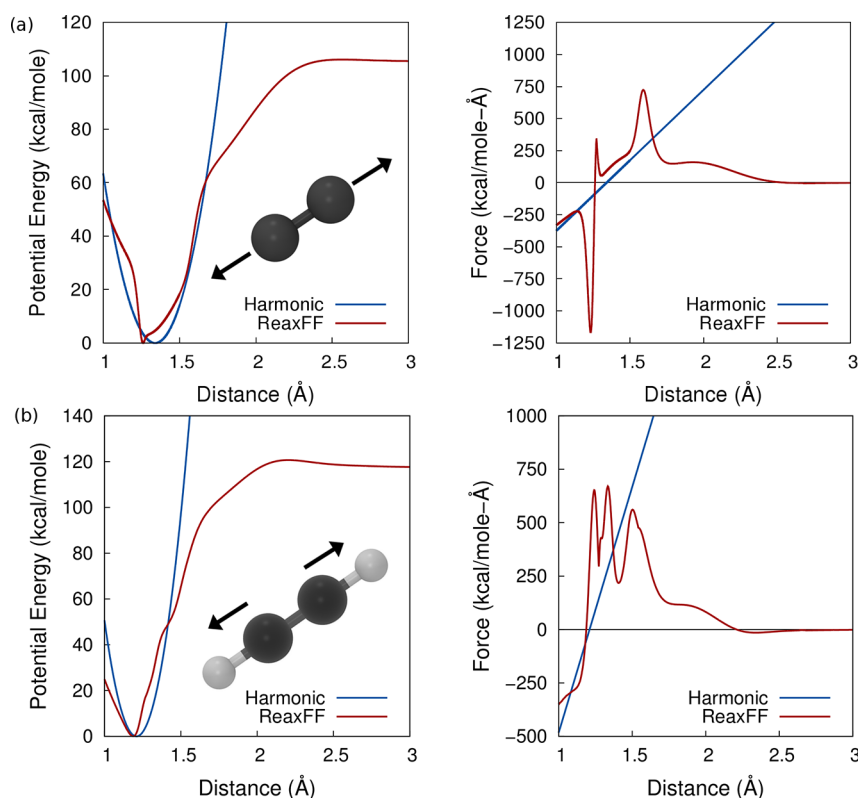
Molecular modeling can be used to accelerate the design and development of carbon-based materials. Molecular models give detailed atomic information not easily obtained from physical samples, and they provide precise control over environmental variables in the simulation. Traditionally, researchers modeled atom–atom interactions using molecular dynamics (MD) with fixed-topology force fields where bonds are defined at the beginning of a simulation and remain fixed throughout the simulation. However, since bond dissociation and formation are critical steps in the formation of carbon-based materials from a reactive gas, a new generation of force fields, such as the recently developed Reax Force Field<sup>13</sup> (ReaxFF), are required to simulate these material systems. The ReaxFF has the capacity to model bond dissociation and formation in carbon-based materials.

In the ReaxFF, the potential energy is defined as a function of bond order with energy penalties for nonequilibrium configurations. Parameters for the ReaxFF functions are developed by first simulating reactions that are expected to occur in a system of interest using computationally demanding *ab initio* methods. ReaxFF parameters are then determined that minimize differences between the *ab initio* and ReaxFF potential energies. Different ReaxFF parameter sets have been developed for a variety of systems. Parameter sets developed have been shown to accurately describe bond dissociation and formation for systems including oxidation of hydrocarbons,<sup>14</sup> catalytic formation of nanotubes,<sup>15,16</sup> shock waves in polymers,<sup>17</sup> and many more carbon-based systems.<sup>18–26</sup> However, a variety of ReaxFF force-field parameter sets and simulation parameters have been reported in these studies, and it is unclear what combination of parameter sets and simulation conditions should be used for carbon-based reactive gases.

The objective of this study is to determine the modeling parameters necessary for the accurate simulation of carbon-based reactive gases using the ReaxFF. A parametric study is performed by monitoring the response of C, C<sub>2</sub>, C<sub>4</sub>, CH, C<sub>2</sub>H<sub>2</sub>, and C<sub>4</sub>H<sub>4</sub> systems modeled using various simulation time steps, simulated temperatures, and ReaxFF parameter sets. A description of the ReaxFF is followed by a description of the parametric study modeling details. The results of the study identify the maximum usable time step length, beyond which the simulation results spuriously depend on the value chosen. The results also indicate that choice of temperature and parameter set can have a significant effect on the simulation results.

Received: June 13, 2012

Published: July 25, 2012



**Figure 1.** Comparison of the potential energy and force gradient between the ReaxFF and a generic harmonic potential for (a) a C<sub>2</sub> molecule (with a harmonic force constant of 549.0 kcal/mol and equilibrium bond distance of 1.34 Å) and (b) acetylene (with a harmonic force constant of 1150 kcal/mol and equilibrium bond distance of 1.21 Å).

## 2. REAXFF

The molecular potential energy defined by many traditional force fields is composed of contributions from bond stretching, bond-angle bending, dihedral torsion, van der Waals interactions, electrostatics, and hydrogen bonding. Usually, these energy contributions are a function of the distance between the interacting atoms. In ReaxFF, these terms, instead, are a function of the bond order, which goes to zero as the distance between the atoms is increased. In addition to these typical contributions, the ReaxFF has several additional energy terms to describe other atomic interactions. For example, the ReaxFF includes energy terms for conjugated systems, angles with a double bond, lone pair electrons, over and under coordinated atoms, a special term for the C<sub>2</sub> molecule, and potentially other terms, depending on what equations are specified for a particular ReaxFF parameter set.

The time step required to get accurate results with the ReaxFF may be quite different than those used with traditional force fields. The proper choice of time step is highly dependent on the stiffest portion of the force gradient experienced by the atoms during MD simulations. In traditional force fields, the stiffest molecular interactions of a system in equilibrium are harmonic bond stretches, which exhibit a linear force–distance relationship for all deformation magnitudes. With the ReaxFF however, because bonds can break and form, the force between interacting atoms is nonlinear. In addition, for specific molecular systems, like all-carbon systems, the force gradient can be much steeper than those in traditional force fields. In addition, ReaxFF incorporates the EEM<sup>13</sup> charge equilibration method to handle charge transfer between atoms as reactions take place. While not important for the all-carbon and

hydrocarbon systems being investigated in this study, charge transfer in polar systems can also be substantially affected by time step size. Because of these factors, the selection of a MD time step that results in accurate predictions is not straightforward. For example, consider the energy-deformation and force-deformation curve of the bond in C<sub>2</sub> and acetylene molecules, as shown in Figure 1 for both the ReaxFF and a typical harmonic alkene carbon–carbon bond. It can be seen that the energy slope near the equilibrium bond distance is much greater for the ReaxFF, compared to the typical harmonic potential. It also shows that, as the bond in both molecules is stretched, the slope of the ReaxFF force curve varies significantly away from the equilibrium distance, in contrast to the constant slope of the harmonic potential force curve. As a result, the maximum MD simulation time step size that may be used with the ReaxFF is expected to be much smaller than that for a traditional force field containing a typical harmonic bond.

With traditional force fields, once the system is near equilibrium, the time step size can be validated by running a simulation in the microcanonical ensemble. If the time step is too large, the total energy of the system will not be conserved, typically increasing over the course of the simulation. In some simple cases, this method can also be applied to the ReaxFF by temporarily modifying the parameter set to disable favorable reactions, causing the initial system to remain in equilibrium, acting like a fixed-topology force field. However, this method only verifies the time step size for molecules present in the initial system. Once the system is allowed to react, new bonds and molecules will form, which may require smaller time steps. An alternative approach for verifying the time step size when

using ReaxFF is to run simulations of identical systems under identical conditions with different simulation time step sizes. There will be a critical time step after which all smaller time steps will result in the same response in the system. This critical time step will allow for the most efficient and accurate simulation of a particular system while the using the ReaxFF. This approach has the advantage that it will sample all molecules present throughout the reaction process.

### 3. PARAMETRIC MODELING PROCEDURE

For this parametric study, six different initial gas molecules were included. Three pure carbon systems were simulated: C, C<sub>2</sub>, and linear C<sub>4</sub>. In addition, three corresponding radical hydrocarbons were also simulated: CH, C<sub>2</sub>H<sub>2</sub> with both hydrogen atoms bonded to a single carbon atom, and C<sub>4</sub>H<sub>4</sub> (Figure 2). These small radical carbon and hydrocarbon molecules are expected to be present in various reactive gas manufacturing processes, if only transiently.

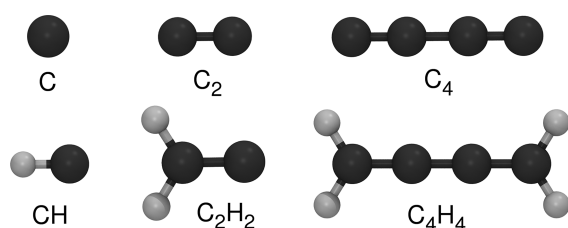


Figure 2. Initial gas molecules simulated.

Two ReaxFF parameter sets were used to model the reactions. The parameter set of Nielson et al.<sup>15</sup> (henceforth referred to as Nielson) was originally parametrized for reactions expected in nanotube formation and growth from transition-metal atoms. This parametrization is well-suited for small cyclic and acyclic carbon structures, graphite, various graphenes, various nanotubes, fullerenes, and hydrocarbon reactions. This parameter set is also well-suited for reactions of carbon with nickel, copper, and platinum atoms. The parameter set of Chenoweth et al.<sup>4</sup> (henceforth referred to as Chenoweth) was parametrized for the reactions of small hydrocarbon molecules with oxygen. Other published parameter sets for ReaxFF exist; however, the Chenoweth and Nielson parameter sets are the most recent parameters useful for either oxygen or transition-metal reactions, respectively, with all-carbon and hydrocarbon molecules.

Three different temperatures were modeled as part of the parametric study: 300, 1500, and 3000 K. This temperature range was selected based on the range of temperatures that carbon-based structures can be exposed to during typical synthesis and operating conditions. The Berendsen thermostat was used to maintain the temperature in the MD models with a damping coefficient of 5 fs.

Five different simulation time steps were selected: 0.4, 0.2, 0.1, 0.05, and 0.025 fs. These time steps encompass the range of typical time steps reported in the literature for a wide range of force fields. It is expected that time steps as large as 0.4 fs result in faster simulation times, but may cause divergent results. A time step as small as 0.025 fs is expected to take ~16 times more CPU hours, but will produce accurate simulations. It is expected that there is a critical time step between 0.4 fs and 0.025 fs where further decreases in time step size do not change the simulation results.

A three-dimensional (3D) periodic MD simulation box was constructed for each initial gas molecule, parameter set, temperature, and time step combination. Each molecular simulation was conducted in a cubic cell with sides 90.0 Å long. Molecules were added to the cell until the total number of carbon atoms in the system reached 900, resulting in a total density of 0.02455 g/cm<sup>3</sup> for the pure carbon systems and 0.02663 g/cm<sup>3</sup> for the hydrocarbon systems. The initial state of each system was equilibrated by running an NVT simulation of the system for 3 ns at the desired temperature using a modified Amber force field. In this force field, parameters were modified to produce bond lengths similar to those of ReaxFF, and only the repulsive portion of the van der Waals term was included. This step prevented the initial state from including high-energy configurations such as overlapping atoms. The trajectories of the atoms were saved at 1, 2, and 3 ns and subsequently used to establish three different simulation samples for each time step, temperature, parameter set, and initial molecule combination, resulting in a total of 540 MD models. The fixed topology force field was then replaced with the ReaxFF. Subsequently, the system energies were minimized and the simulations were run for 500 ps, 1 ns, or 1.5 ns, depending on what duration was required for the reactive system to reach equilibrium. The system energies were recorded at regular intervals throughout each ReaxFF simulation. Simulations were performed on several high-performance computing systems using the LAMMPS<sup>27</sup> software, which includes an implementation of the ReaxFF code. An example of an equilibrated system is shown in Figure 3.

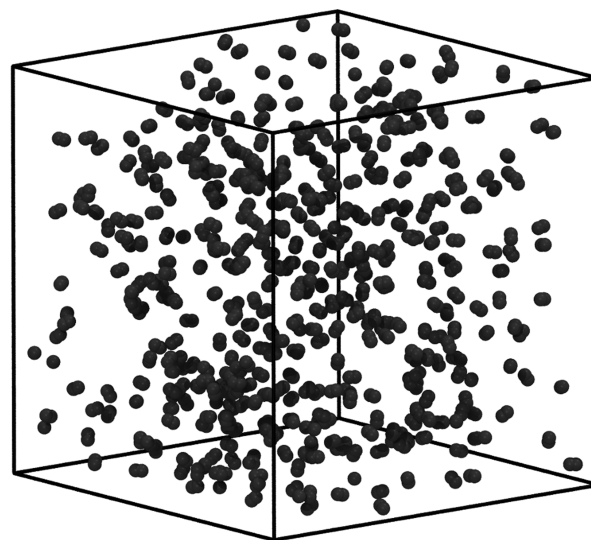
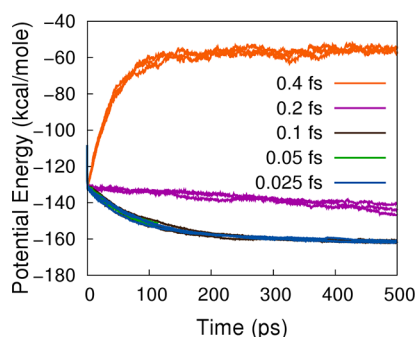


Figure 3. Equilibrated system of C<sub>2</sub> molecules at 300 K.

### 4. RESULTS AND DISCUSSION

An example of the influence of time step size on the simulated evolution of the reactive carbon gases is shown in Figure 4. This figure clearly shows that there is a maximum time step size below which the potential energy curves show close agreement (0.1 fs). For larger time step sizes, the corresponding potential energy curves diverge from these results. It is also clear from this figure that simulations run with different initial configurations show close agreement for a given set of parameters. For each combination of temperatures and initial gas molecules, the corresponding maximum time step sizes are



**Figure 4.** Influence of time step on potential energy convergence for a system of  $C_4$  initial gas molecules at 1500 K using the Chenoweth parameter set.

listed in Tables 1 and 2 for the Chenoweth and Nielson parameter sets, respectively.

**Table 1. Maximum Time Step Size for Various Reactive Carbon Gases at Different Temperatures Using the Chenoweth Parameter Set**

molecule	Maximum Time Step (fs)		
	300 K	1500 K	3000 K
C	0.1	0.1	0.1
$C_2$	0.1	0.1	0.1
$C_4$	0.2	0.1	0.1
CH	0.2	0.1	0.1
$C_2H_2$	0.2	0.2	0.1
$C_4H_4$	0.4	0.2	0.1

**Table 2. Maximum Time Step Size for Various Reactive Carbon Gases at Different Temperatures Using the Nielson Parameter Set**

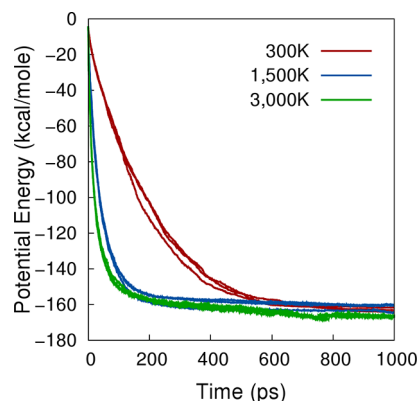
molecule	Maximum Time Step (fs)		
	300 K	1500 K	3000 K
C	0.1	0.1	0.05
$C_2$	0.1	0.1	0.05
$C_4$	0.1	0.1	0.05
CH	0.2	0.1	0.1
$C_2H_2$	0.2	0.1	0.1
$C_4H_4$	0.2	0.1	0.1

The data in Tables 1 and 2 indicate that, for a majority of the simulated conditions, a time step of 0.1 fs was sufficiently small to yield reliable results. The data also indicate that, as the simulation temperature increases, smaller time steps are generally necessary for convergent results. Running simulations at very high temperatures results in increased sampling of large-amplitude bond vibrations. As the potential energy gradient is nonlinear in this region, shorter integration time steps are required to ensure numerical stability and reliable simulation results.

The data in Tables 1 and 2 also indicates that, generally, the pure carbon systems require smaller time steps than the hydrocarbon systems. There are several possible explanations for this. First, there is a  $C_2$  correction term used by the ReaxFF when the  $C_2$  molecule is present. For the hydrocarbon systems, it is unlikely that there are significant numbers of  $C_2$  present at any given time. Therefore, the  $C_2$  correction term can influence the required time step size for pure carbon systems but is

unlikely to have a significant effect of the hydrocarbon systems. Second, the higher mass of the hydrocarbon systems could alter the natural vibrational frequencies of the molecules, thus changing the time step size necessary for accurate simulation. Finally, the presence of hydrogen in the hydrocarbon molecules could cause the molecules to be more chemically stable, resulting in a force gradient with fewer sharp spikes and thus higher minimum time steps.

Figure 5 shows a typical plot of the influence of simulation temperature on the evolution of carbon reactive gases. The



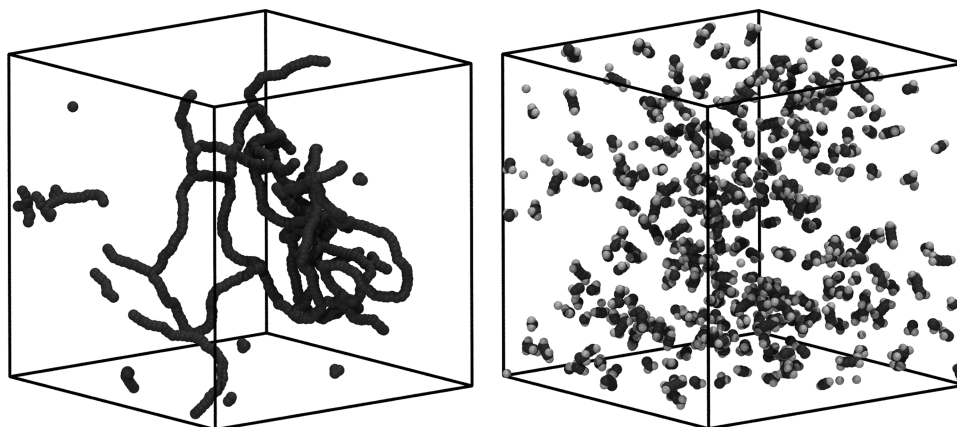
**Figure 5.** Influence of temperature on potential energy convergence for an initial gas of C atoms using the Nielson parameter set.

potential energy generally shows a more rapid approach to its equilibrium value for higher temperatures, indicating that the reaction rates increase with increasing temperature. Also, the results are reproducible, as demonstrated by the similar response of the three different simulation samples at each temperature. The same trends were observed for other initial gas molecules considered in this study. For the pure-carbon systems, the potential energies converged to  $-148$  to  $-160$  kcal/mol when using the Chenoweth parameters and  $-160$  to  $-180$  kcal/mol with the Nielsen parameters. For the hydrocarbon systems the potential energies converged to  $-108$  to  $-120$  kcal/mol when using either parameter sets. The variation in final potential energies decreases further for increasing temperatures with final potential energies of different initial gases within 4 kcal/mol of each other at 3000 K. For all of the pure carbon systems, the equilibrium structures are mostly long linear-branched carbon molecules with a small number of stable cyclic  $C_3$  molecules (Figure 6). The final structure of the hydrocarbon systems consisted primarily of short linear hydrocarbon molecules with hydrogen atoms terminating the ends of the carbon chains (Figure 6).

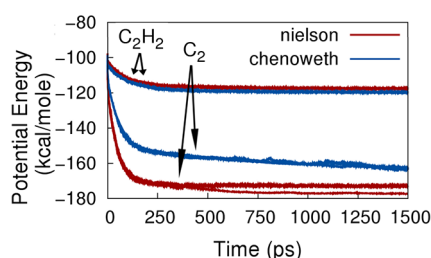
Figure 7 shows the influence of the two different ReaxFF hydrocarbon parameter sets on the potential energies of an initially pure  $C_2$  system and an initially pure  $C_2H_2$  system, both at 1500 K. From the figure, it is clear that, for the  $C_2$  system, the Nielson parameter set results in greater initial reaction rates than the Chenoweth parameter set. Similar trends have been observed for the other pure carbon systems and the CH system at all temperatures. From Figure 7, it is also clear that, for the initially pure  $C_2H_2$  system, the predicted reaction rates for the two parameter sets are almost identical. A similar trend was observed for the  $C_4H_4$  system at all temperatures.

Figure 8 shows a typical example of the influence of the initial gas species on the reaction rates of the molecular system. From the figure, it is evident that starting with single carbon

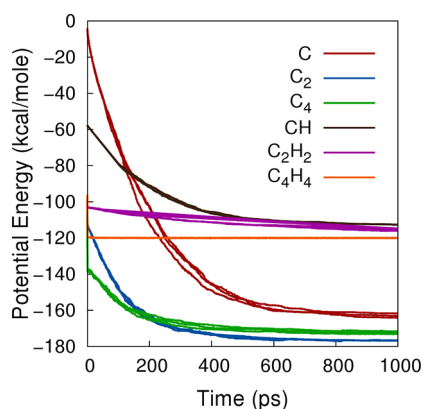




**Figure 6.** Final structures for initial gas of carbon atoms at 3000 K with the Nielson parameter set (left) and an initial gas system of  $C_2H_2$  at 3000 K with the Chenoweth parameter set (right).



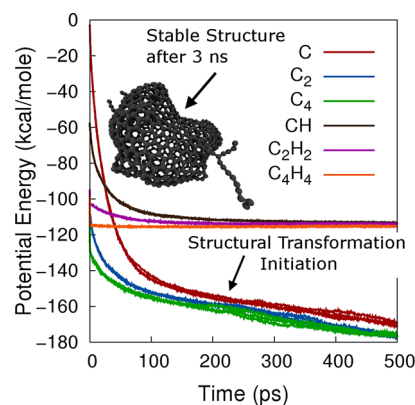
**Figure 7.** Influence of parameter set on potential energy convergence for initial gas of  $C_2$  and  $C_2H_2$  molecules at 1500 K.



**Figure 8.** Influence of initial gas molecules on potential energy convergence, using the Nielson parameter set at 300 K.

atoms yields the fastest initial reaction rate. Because of the high initial potential energy, there is a significant driving force to react very quickly to form  $C_2$ ,  $C_3$ ,  $C_4$ , and higher-order carbon structures. Also, since there are no bond vibrations for C, all of the kinetic energy in a single carbon atom is translational. As the single carbon atoms react to form higher-order carbon chains with more bonds, more of the translational potential energy is transformed to bond vibration potential energy. As the translational energy of the molecules decreases, the kinetic energy barriers to lower energy states become more difficult to overcome. It is also important to note that all of the pure carbon systems converge to a similar potential energy in the final state, regardless of the initial molecular type. The same observation can be made about the hydrocarbon systems.

It is interesting to note that, for the Chenoweth parameter set at 3000 K for all of the pure carbon systems, a structural transformation was observed at  $\sim 250$  ps, as shown in Figure 9.



**Figure 9.** Structural transformation predicted in pure carbon systems, as indicated by a sudden decrease in the potential energy near 250 ps.

This transformation is characterized by the formation of large graphitic particles, instead of the long linear carbon chains that the other simulation parameters produced. It is expected that, at the transition point, a small ring forms that can act as a nucleation site for a larger graphitic structure. This finding is significant because it demonstrates the ability of the ReaxFF to predict the formation of similar carbon structures, such as graphite, buckyballs, and carbon nanotubes, with specific simulation parameters. Similar observations have been made using *ab initio* simulations.<sup>28–30</sup>

## 5. CONCLUSIONS

The results in this study indicate that simulations of carbon-based reactive gases using the Reax Force Field (ReaxFF) are highly sensitive to the simulation parameters. In particular, it is clear that, for pure carbon and hydrocarbon gases simulated at 3000 K, a time step of 0.05 fs should be used, whereas for lower temperatures (300 and 1500 K), time steps of 0.1 fs are sufficient for accurate simulation. The results also indicate that the selection of parameter set may also have a significant influence on the simulation results. While the Nielson and Chenoweth parameter sets predict similar equilibrated potential energies, the reaction rates for the Nielson set are faster than

those for the Chenoweth set for the pure carbon systems. Although the Nielson and Chenoweth parameter sets usually result in simulations that predict the same equilibrated structures, it was observed that, for pure carbon systems simulated at 3000 K, the Chenoweth parameter set yielded the formation of large graphitic structures that the Nielson parameter set did not. This may indicate that the Chenoweth parameter set may be more appropriate for MD simulations in which the growth of graphitic structures is investigated.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Complete results of the parametric study are included in Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This research was funded by NASA under the Revolutionary Technology Challenges Program (Grant No. NNX09AM50A).

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