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PARAMETRIC STUDY OF REAXFF SIMULATION PARAMETERS FOR MOLECULAR DYNAMICS MODELING OF REACTIVE CARBON GASES

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PARAMETRIC STUDY OF REAXFF SIMULATION PARAMETERS FOR
MOLECULAR DYNAMICS MODELING OF REACTIVE CARBON GASES

By

Benjamin D. Jensen

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Preface

Select text from chapters 2, 3, 4, and 5 and Figures 3.1, 3.2, 4.1-4.7 adapted with permission from Jensen, B. D.; Bandyopadhyay, A.; Wise, K. E.; Odegard, G. M., *Journal of Chemical Theory and Computation* **2012,** *8* (9), 3003-3008[1]. Copyright 2012 American Chemical Society.

Ananyo Bandyopadhyay provided helpful instruction to me as I learned the fundamentals of molecular dynamics. He provided example input scripts and advice. I met biweekly with Kristopher Wise where he advised how to make the project most relevant to NASA's objectives. Kris Wise also made comments and corrections to the manuscript. Gregory Odegard advised me over the course of the project and wrote and corrected portions of the manuscript.

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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.

Chapter 1: Introduction

Translation of properties of nanoscale constituents to bulk sized materials presents immense opportunities and challenges. Nanoscale constituents can have properties orders of magnitude better than those of current materials. Because of this, nanostructured materials are expected to play an important role in future structural materials including on aircraft and spacecraft.

The February 2010 "National Aeronautics Research and Development Plan" set research objectives for future commercial aircraft.[2] The goals set by the government include substantial reductions in energy consumption by commercial aircraft. NASA set specific goals to reduce energy use by 2030 shown in Table 1.1. Current metal materials and even carbon fiber reinforced composites are not capable of meeting the demands of future aircraft. Breakthroughs in the development of lightweight nanostructured materials are expected in the upcoming decades that will lead to their wide scale use for structural aerospace components.

Table 1.1 NASA third generation aircraft performance goals

	Goal
Reduce environmental noise	71 dB
Reduce NOx emissions	75%
Reduce fuel burn	70%
Runway length	50%

The carbon nanotube is a recent discovery that has many remarkable properties. The discovery of carbon nanotubes has been largely credited to Sumio Iijima in 1991,[3] although it has been since noted that images and descriptions of carbon nanotubes had been previously published without fanfare.[4] The mechanical properties of carbon

nanotubes are game-changing, with stiffness around 1.0 TPa, ultimate strength anywhere from 50-120 GPa and fracture strain between 15% and 19%[5]. If a bulk material could be made with even half of the strength and stiffness of an individual nanotube then the resulting material would still have a stiffness to weight and strength to weight ratio an order of magnitude better than current state of the art alloys and composites.

1.1 Motivation

Carbon based nanostructured materials are particularly promising for aerospace structural applications. These components are necessarily stiff, strong, ductile, and lightweight. Most structural components today are made from metal alloys. Because of their extensive use over a long period of time the metals used are near their potential maximum performance. Comparatively carbon based nanostructured materials are in their infancy and, while their properties are not currently better than metal alloys, have the potential to be several orders of magnitude stronger and stiffer than current metal components once fully developed.

There are many nanoscale particles that may be useful as nanoscale constituents. Among them are the carbon nanotube, graphene, nano-diamond, nano-onions of carbon and buckyballs.

Carbon nanotubes are a crystal form of carbon consisting of sp^2 bonds in a hexagonal sheet arrangement wrapped into a tubular shape. Carbon nanotube diameters are in the nanometer range and can have lengths into the micrometer range. The strong carbon-carbon bonds, crystal arrangement, and reinforcing cylindrical shape make it one of the strongest materials discovered. The hollow core in carbon nanotubes makes it a very low-density material, ideal for aerospace applications. Carbon nanotubes can also possess interesting electrical characteristics. Depending on the bonding arrangement, carbon nanotubes can be either insulating or conductive. Conductive structural fiber multifunctional components can reduce weight by eliminating conventional wiring, and also provide new opportunities like conductive tethers for new green technologies such as windmill kites and spacecraft such as the TSS-1R Tethered Satellite System.

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,[6] chemical vapor deposition,[7, 8] pulsed arc discharge deposition,[9] plasma deposition,[10-13] pulsed laser deposition,[6, 14] laser ablation, combustion,[15, 16] and ion beam irradiation[17] 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[18] (ReaxFF), are required to simulate these material systems. The ReaxFF has the capacity to model bond dissociation and formation in carbon-based materials.

ReaxFF parameter sets developed have been shown to accurately describe bond dissociation and formation for systems including oxidation of hydrocarbons,[19] catalytic formation of nanotubes,[20, 21] shock waves in polymers,[22] and many more carbon-based systems.[23-31] 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.

1.2 Objective

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_2, C_4, CH, C_2H_2, and C_4H_4 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.

Chapter 2: Background

This chapter will give an overview of research areas important to modeling reacting carbon-based gasses.

2.1 Molecular Modeling

Molecular modeling simulations have been used extensively to investigate atomic scale phenomenon for decades. Initially, when computers had minimal computational power, very small system were simulated using simple interaction potentials. Simulations of halogens and diatomic gases being some of the simplest performed. As computational power increased over time molecular modeling became more common and models became larger and more complicated. State-of-the-art molecular models can contain millions of atoms, use complicated interaction potentials and for hundreds of nanoseconds.

Ensembles

Molecular modeling often involves sampling states in a defined ensemble. An ensemble is a collection of all possible positions and momentum that may be experienced by the atoms in the system in a defined state. The combination of all positions and momentums of the atoms in a system is referred to as phase space. An ensemble is an area of phase space that satisfies defined thermodynamic values such as a fixed temperature, volume, pressure, or energy. Common ensembles used in molecular modeling are detailed below.

Canonical (NVE)

Energy within the system is conserved, oscillating between potential energy of the bonds and the atoms kinetic energy. In addition to fixed total energy the volume and number of atoms of the system is constant.

Micro Canonical (NVT)

The system is allowed to change total energy by exchanging kinetic energy with a theoretical surrounding heat bath. In this ensemble the temperature, number of atoms, and volume are constant.

Isobaric-isothermal (NPT)

The volume of the system is adjusted to maintain a set pressure. The number of atoms is fixed and temperature of the system is held constant like in the micro canonical ensemble.

Molecular Dynamics

Molecular dynamics (MD) is a method of sampling portions of phase space. MD simulations employ Newton's second law to move atoms discreetly in time. In a MD simulation thermodynamic averages of an ensemble can be calculated by averaging over points in time that are far enough apart to be statistically uncorrelated. This makes MD similar to Monte-Carlo simulations where new positions are selected according to thermodynamic probability and a random number, instead of following a trajectory in time.

In MD there are several algorithms for controlling the temperature and pressure of the system. The most common methods are described below.

Nose-Hoover Thermostat and Barostat

This algorithm scales the velocities to the desired temperature in a way that creates a Gaussian distribution. This method is the only thermostat to have a strict statistical mechanics derivation and is most likely to generate momentum in the desired ensemble.

Berendsen Thermostat and Barostat

This method scales all velocities proportionally by the same factor to achieve the desired temperature. Used extensively for ReaxFF because it is known to better control very large velocities often found in rapidly changing systems such as reacting or non-equilibrium systems. This algorithm is also much simpler to code and is therefore common in small MD codes.

Langevin Thermostat

This thermostat scales the velocity and also adds a force in a random direction, simulating collisions with solvent molecules. This results in random-walk type diffusion of particles under the correction conditions. This thermostat also results in a non-Gaussian distribution of velocities, favoring the average temperature and reducing the magnitude of higher velocities making it good for equilibrating bad systems.

Thermodynamic Fluctuations

It is important to note that macroscopic thermodynamic properties are averages of many atoms. For example temperature is an average of the velocities of many atoms. Pressure is the average of the virial of many atoms, and potential energy is the average of the potential of many atoms. Typical thermodynamic measuring equipment such as barometers and thermometers are large, containing many moles of atom, therefore the thermodynamic properties are averages of many moles of atoms. However, with molecular modeling simulations the number of atoms may be anywhere from tens of atoms to at most millions of atoms, many orders of magnitude less than even a single mole. Therefore it is expected that averages of the velocities in an MD simulation will vary significantly in time around the average value. The magnitude of the fluctuations is directly related to the total number of atoms. Very small systems of tens of atoms will have massive fluctuations in thermodynamic values, while systems of tens of thousands will have smaller fluctuations and systems of millions of atoms will have even smaller fluctuations. However even with millions of atoms thermodynamic values will still fluctuate. Therefore thermodynamic fluctuations are a natural product of the method and are not necessarily an indication of a problem.

2.2 The Reax Force Field

Traditionally researchers have used force fields with fixed bond topologies such as AMBER, OPLS, CHARM, and COMPASS to model covalent systems, where bonds are defined at the beginning of a simulation and remain fixed throughout. Often these force fields use simple harmonic functional forms to describe bonded interactions, assuming bonds are not stretched far from equilibrium. These models and their corresponding assumptions are applicable for modeling many equilibrium systems such as polymers and proteins. However use of these force fields restricts their use to equilibrium non-reacting systems. Investigations of systems where bonds break or form are important to many researchers. In particular use of reactive force fields expands to scope of materials research, allowing growth of a material during manufacture to be simulated.

The Reax Force Field (ReaxFF) is a new generation bond-order force field developed by Adri van Duin et al. at Cal Tech and first published in 2001.[32] ReaxFF is the most recent of a long history of reactive force fields used in molecular dynamics, and is designed to be highly transferable to diverse systems such as covalent, ionic, and metallic and is under active development with parameter sets for new systems being published every year since its release. ReaxFF is designed to describe bond dissociation and other higher order effects, typically found using DFT methods, but at significantly less computational expense allowing for the simulation of systems orders of magnitude larger with similar accuracy.

History of Reactive Force Fields

Morse Bond Potential

Previously other force fields have been developed that allow for breaking and forming of bonds. One of the simplest potentials is the Morse potential developed in 1929 by Philip Morse.[33, 34] The Morse potential is two-body force field in that only the distance between each pair of interacting atoms affects the energy of each bond, irrespective of other nearby atoms. In practice the Morse potential is used similarly to fixed-bond force fields where bonds are selected at the beginning of a simulation. However as a Morse bond is

stretched, the bond can dissociate and the force between the atoms goes to zero. The shape of the bond energy dissociation curve is fixed by the form of the potential with the minimum potential energy, dissociation energy, and equilibrium bond distance set by the user. Near equilibrium the Morse potential matches a harmonic potential. This potential is most useful for diatomic molecules, which it was originally use to describe, as there is no easy way to add simple angle or dihedral interactions that also dissipate as the bond dissipates.

Lennard-Jones

Later in 1931 Lennard-Jones proposed his two-body "12-6" potential energy form to approximate van der Waals interactions between atoms[35]. The Lennard-Jones functional form is two-body term is used to describe the long-range van-der-Waals atomic interactions, and not the covalent bonding of the Morse potential. The Lennard-Jones form was used in describing systems where non-bonded energies dominate, like liquids or noble gases.

Bond Energy - Bond Order Method

Harold Johnston and Christopher Parr in 1963 applied Pauling's bond order, which states that there is a direct correlation between bond length and bond order, to a potential form for hydrogen transfer.[36] The critical principle is that the total bond order of the entire system is conserved, even when a bond has been greatly separated. The limitation of this potential is that it can only be used to describe rate constants for hydrogen transfer reactions. However the introduction of conserved bond order to describe reactions was a useful assumption used in the creation of later force fields.

The Addition of Three-Body Terms

In order to describe a larger set of states than potentials with only single and two-body terms, the two body energy terms were expanded to include higher orders of body terms. These include the potentials of Stillinger and Webber, Pearson et al, and Biswald and Hamann.[37-39] The Stillinger-Webber and Pearson models included two-body and three-body terms that were parameterized to reproduce specific properties of silicon. Biswald

and Hamann added a large array of states to their fitting database and tried to fit their parameters very generally to all these states. Their model, though, did not give good results, and therefore the three-body term was not enough to model the diverse set of states for silicon, and in particular non-tetrahedral states of silicon.

Abell Bond Order Function

In 1985 Abell proposed that the bond order of an atom was dominated by the number of near neighbors.[40] Near neighbors are atoms within the covalent bonding distance from that atom. Abell's functional form added an adjustable parameter to the shape of the Morse potential to better describe some reactions. For bond distances less than the equilibrium the Abell form is identical to the Morse potential.

The Teroff Potential

Tersoff, in 1986, identified the weaknesses of higher body-order terms and took the ideas of Abell and Morse to create a potential to model silicon.[41] Tersoff's great addition was to split the potential into a repulsive and attractive part and multiply the attractive part by the bond order. The bond order is a function of the number of nearest neighbors, the angle between neighbors, and the distance to the near neighbors. By making the bond order dependent on the geometry, his model was able to achieve better computational scaling and greater simplicity than by adding a three-body or, four-body potential. The attractive and repulsive terms of the Tersoff potential are multiplied by a cutoff function so that the bond energy goes to zero for large deformations. Since long-range forces and charges do not play a significant role in silicon structures they were not included, which makes it difficult to generalize the Tersoff potential to many systems. Also the shape of the dissociation curve is not adjustable. However with this form Tersoff was very successful in simulating a large number of Silicon and similar systems.

Brenner Parameterization of the Teroff Form (REBO)

In 1990 Brenner published a parameterization of the Tersoff potential used to describe Chemical Vapor Deposition (CVD) of hydrocarbons on a diamond surface.[42] This potential is commonly known as the Reactive Empirical Bond Order (REBO) potential.

In addition to parameterizing the Tersoff functional form, he also included terms to differentiate conjugated systems from linear molecules. For example the Brenner potential can differentiate between the resonant double carbon-carbon bond in graphite and the double carbon-carbon bond in $(CH_3)2C=C(CH_3)$. Brenner also included a term to improve the accuracy of radicals. With this term vacancies in a diamond lattice could not be accurately modeled.

AIREBO

In 2000, after the successful implementations and adoptions of the Brenner potential to many hydrocarbon systems, Stuart et al. added non-bonded interactions and single-bond dihedral energies to the Brenner potential in order to better simulate systems like liquids and thin films where these energies play a larger role.[43] This is commonly called the Adaptive Intermolecular REBO potential (AIREBO). The long-range energies are represented by a Lennard-Jones equation. This leads to unrealistic repulsion at short distances. However for many systems this is not important. Lennard-Jones interactions are also not included in atoms that are within four bonds and on the same molecule.

The Reax Force Field

Then in 2001 a new reactive potential form was introduced by van Duin et al. that aimed to create a reactive force field functional form that corrected many of the problems of the Brenner-Tersoff style potential. Like Tersoff, Abell, and Brenner, ReaxFF has a direct distance - bond order relationship. This force field's potential energy curve is a composite of many terms including bonds, angles, dihedrals, conjugation, over/under coordination, van-der-Waals, electrostatics and more. This form allows for the shape of the bond dissociation curve to be fitted to QM results. In addition when the ReaxFF is parameterized long-range forces are included from the start, being parameterized simultaneously along with the other energies as opposed to AIREBO where covalent energies are parameterized first and then long-range energies are parameterized afterwards. In the ReaxFF the QEq charge distribution scheme is used which allows for charges on atoms to change as they react and form new molecules. The original ReaxFF was published along with parameters fit to hydrocarbon reactions, while subsequent

publications have included parameter sets for a wide variety of elements and reactions. The ReaxFF will be discussed more thoroughly later.

Second Generation REBO

In 2002 Brenner updated his original REBO potential with parameters derived from a more extensive training set and modified analytic functions.[44] The long range and dihedral terms for the previous AIREBO potential can also be added to the second generation REBO potential since they are parameterized separately.

Summary

There are two primary reactive molecular force fields that are under active use and development for describing covalent carbon systems. These are the Brenner-Tersoff form force fields, and the ReaxFF potential. Both are built on a long evolution of earlier potentials dating back to the 1920s. Both Brenner-Tersoff and ReaxFF are based on the Abell distance-bond order relationship.

Other Higher Order Methods

Other methods of simulating materials are Density Functional Theory (DFT) and *ab initio* simulations. These are expected to be more accurate than the molecular force fields, however they are also significantly more computationally expensive so they are more appropriate for much smaller systems.

ReaxFF Potential Energy Definitions and Explanations

The ReaxFF potential energy function is defined as the sum of many individual energy terms. Some of the terms are typical of any force field including fixed topology force fields such as potential energy terms from bonds, angles, dihedrals, van der Waals, electrostatics, and hydrogen bonds. However with ReaxFF instead of these terms being directly dependent on the distance between atoms, these terms are dependent on the bond order which varies continuously between single, double, and triple bonds and gradually goes to zero as the distance increases. In addition to the typical terms mentioned ReaxFF includes contributions from over and under coordinated atoms (radicals, and

oversaturated valences), lone pair electrons, extra rigidity for angles that include a covalent double-bond, C_2 triple bond destabilization energy, three body conjugation such as $-NO_2-$, and four body conjugation such as benzene.

Parameterization of ReaxFF

A significant advantage of the ReaxFF is that the functional form of the potential energies is very broad and encompasses a variety of bonding situations such that it can be parameterized for diverse systems with metallic, ionic, and covalent bonding. While the various parameterizations for ReaxFF are made to be as broadly applicable as possible, care must be taken to ensure that the selected parameter set reproduces the desired properties. ReaxFF parameterizations are developed by generating a database of coordinates for crystal structures and molecules and their corresponding energies using highly accurate QM methods and then tweaking the ReaxFF parameters until the difference in ReaxFF and QM energies is minimized for each set of coordinates. This database of coordinates and QM energies is called the training set, since it is used to "train" the ReaxFF to reproduce the QM results in the database. ReaxFF training sets typically include points along the bond dissociation curves for a variety of molecules, relative potential energies of stable and radical molecules, equation of state (EOS), and lattice constants for stable and unstable crystal structures. Inclusion of the EOS indirectly includes elasticity constants in the parameterization. When a parameter set is generated different weighting factors are given to each data point. With this weighting scheme critical reactions can be forced to be match well, potentially at the expense of less critical reactions. A single point minimization technique is used determine the parameters, where single parameters are minimized sequentially until the overall energy difference converges to a minimum. Selecting an efficient and accurate minimization steps and parameters can be quite difficult and require substantial expertise.

When selecting a parameterization for ReaxFF it is important to keep in mind that the properties desired, in addition to the elements in the parameterization are important. For example there are several parameterization that include carbon, but for different situations such as shock waves in polymers,[22] transition metal catalyzed nanotube

formation,[45] absorption of carbon in nickel clusters,[20] oxidation and combustion,[46] in addition to the original hydrocarbon parameter set.[32] Each of these parameterizations includes different carbon reactions in the training set. Currently, no EOS for carbon crystals such as diamond and graphene has been included in a training set. Therefore it is important to verify the accuracy of the parameter set for elasticity of carbon crystals if that is the desired property. ReaxFF parameter sets are usually published in a standard format in a text file in the supporting information section of the paper. The text file can be read by the stand-alone Fortran code made by the ReaxFF developers, a parallel C++ code developed at Purdue or using the generic MD software LAMMPS that has both the Fortran and C++ implementations included as additional optional packages. Details on the current body of published parameterizations for ReaxFF and their applications are described below.

Relevant Parameterizations for ReaxFF

Generic Carbon Parameters

The ReaxFF was originally published along with parameters suited for a wide variety of hydrocarbon reactions.[32] This paper includes extensive discussion on each equation in the force field. This parameter set reproduced QM values near 4 kcal/mole for heat of formation, bond lengths near 0.01 Å, and angles near 2°. The heat of formation of 110 hydrocarbon molecules, the bonds and angles in 19 molecules, relative potential energies of 11 molecules, and lattice constants for 4 structures. This parameter set forms the base for most future parameterizations, and is shown to be accurate for a diverse set of small hydrocarbon systems.

Then in 2008 Chenoweth et al. created a parameterization for hydrocarbon oxidation, which included previous hydrocarbon reactions in the training set in addition to reactions with oxygen.[46] The parameter set has been used extensively to model a variety of hydrocarbon and oxygen systems since.

In 2011 Liu et al. applied recently developed DFT van der Waals low-gradient to carbon, nitrogen, hydrogen, and oxygen parameters.[47] The van der Waals equation from the original publication is a shielded Morse form. However recently developed DFT methods to more accurately model van der Waals interactions indicated the ReaxFF functional form was inadequate, and a scaling term was added and parameterized. The lattice constant for diamond, polyethylene, and small explosive molecule structures were validated with the new parameters with good results.

Carbon based explosives

The original hydrocarbon training set was extended with nitrogen and oxygen reactions in order to model high-energy materials such as nitramine RDX by Strachan et al.[48] Later this training set was expanded to include unimolecular pathways for the high-energy material TATP[49] and reparameterized. Condensed phases for TATP were also included in the training set. Note that while the original RDX parameterization included all the elements found in TATP, since reactions relevant to TATP decomposition were not included in the training set, it was not accurate, and the training set needed to be expanded. More recently in 2009 Zhang further expanded the training set for thermal decomposition of the explosives TATP and HMX.[27]

Catalyzed fullerene growth

Nielson expanded on the previous hydrocarbon training sets and added reactions of hydrocarbons with single atoms of Co, Cu, and Ni.[45] These transition metal elements are common catalysts in the manufacture of carbon nanotubes. Relative energies of a variety of pure carbon species were added to the training set including graphene, graphite, diamond, a few nanotubes and C_{60}. Small acyclic and cyclic molecules of pure carbon were also included. In this parameter set the energy term C_2 was added to destabilize the triple bond in C_2. While a number of condensed states for carbon were included in this training set, their EOS was not included. Only equilibrium values were included. Later the carbon-nickel interactions were expanded with nickel-nickel interactions and nanotube growth from a nickel particle was simulated by Mueller et al.[20]

Proteins

Rahaman et al. developed ReaxFF parameters for glycine with water.[50] The parameter set included the elements carbon, nitrogen, oxygen, and hydrogen. In addition a bond restraining energy term was added in order to restrain O-H bonds and N***H bonds, forcing proton transfer which was of interest to the authors. This parameter set was tweaked shortly afterwards and used to model proline-catalyzed iminium–enamine conversion.[51]

Other carbon based systems

The organic silicon oxygen were further analyzed and validated in particular the organic silicon interactions by Chenoweth et al. who used it to model the thermal decomposition of the silicone polymer PDMS.[52] PDMS was heated to a variety of maximum temperature and heating rates and the products of the cook off simulation were analyzed.

Silicon based parameterizations

Adri van Duin et al. developed ReaxFF parameters for silicon and silicon oxide.[53] The original hydrocarbon training set was also included as well as silicon and silicon oxide reactions with carbon and hydrogen. Crystal structures of stable and unstable crystal structures of silicon and silicon oxide are included in the training set over a large range of pressures from 500 GPa compression to 10 GPa in tension. After the parameters were developed a silicon and silicon oxide interface was successfully modeled. More recently the silicon-oxide parameter set was expanded to include gas phase molecules and DFT simulations in the original training set were re-run with more accurate recently developed DFT functionals.[54] The silicon training set was also expanded by Naserifar et al. to include reaction found in the thermal decomposition of hydridopolycarbosilane to form a low-density silicon-carbon material.[55]

Metals, transition metal, and other parameterizations

In addition to carbon and silicon parameterizations, the ReaxFF has been applied to a wide array of other elements including metals, transition metals, boron-nitride, and halogen elements. Many of the metal parameterization includes stiffness coefficients and

EOS data in their training sets that allows the parameterization to reproduce mechanical properties well. A significant number of ReaxFF parameterizations for investigating metal surface catalyzed hydrocarbon reactions have been developed primarily by the group of Bill Goddard. Metal alloys, metal oxides, metals for hydrogen storage, cold welding, and even concrete have been studied using the ReaxFF. An overview of all 44 published ReaxFF parameterizations is listed below in Table 2.1.

Table 2.1 Comprehensive list of ReaxFF parameterizations in chronological order

First Author	Elements	Year	Ref.	Notes
Goddard	C H	2001	32	Original publication
Strachen	C H O N	2003	48	RDX explosive
van Duin	Si O	2003	53	Interface properties
Zhang	Al O H	2004	56	Surface properties
Chenoweth	Si O C H	2005	52	PDMS polymer
Cheung	Mg H	2005	57	Hydrogen storage
Han	B N H	2005	58	BN nanotubes for H storage
Han	Li O H	2005	59	Various lithium compounds
Nielson	C H Ni Cu Co	2005	45	Catalyzed nanotube growth
van Duin	C H O	2005	49	TATP and DADP explosives
Goddard	C H O Mo Bi V	2006	60	Catalysts
Ludwig	Pt H	2006	61	Pt surface with hydrogen
Chenoweth	V O C H	2008	62	Catalysts
Chenoweth	C H O	2008	46	Hydrocarbon oxidation
Goddard	C H N O V Mo Bi Nb Te	2008	63	Catalysts
Jarvi	Au	2008	64	General parameters
Raymand	Zn O H	2008	65	Catalysts
van Duin	Y Ba Zr O H	2008	66	Fuel cell electrolytes
van Duin	Y Zr O	2008	67	General parameters
Kua	C H O Cl Sb	2009	68	Self-assembling materials
Zhang	C H N O	2009	27	Explosives
Aryanpour	Fe O H	2010	69	Water purification
Joshi	Au O H	2010	70	Cold-welding
LaBrosse	Co	2010	71	General parameters
Mueller	C H Ni	2010	20	Catalyst
Rahaman	Cu Cl O H	2010	72	Enzymatic and aqueous processes
Raymand	Zn O H	2010	73	Reparameterized to include water
van Duin	Cu O H	2010	74	Protein activation

Weismiller	B H O N	2010	75	Hydrogen storage
Agrawalla	H O	2011	76	Hydrogen combustion
Liu	C H N O	2011	47	Corrected van der Waals term
Jarvi	Au S C H	2011	77	Self-organizing contacts
Rahaman	C H N O	2011	50	Glycine protien in water
Hubin	C H N O	2012	51	Modified for other proteins
Liu	Ca Al O H S	2012	78	Ettringite
Manzano	Ca O H	2012	79	Calcium oxide surface
Narayanan	Li Al Si O H	2012	80	Lithium-aluminum silicates
Shin	Fe Al Ni	2012	81	Alloy properties
Vasenkov	Mo Ni C O N S H	2012	82	High pressure molybdenum alloys
Zou	Fe C H	2012	83	Catalyst
Gouissem	Hf Zr B	2013	84	Ultra high temperature ceramics
Kulkarni	Si O H	2013	54	Expanded/recalculated training set
Naserifar	C Si H	2013	55	Silicon carbon membranes
Song	Al Mo O	2013	85	Explosives

Chapter 3: Parametric Modeling Procedure

For this parametric study, six different initial gas molecules were included. Three pure carbon systems were simulated: C, C_2, and linear C_4. In addition, three corresponding radical hydrocarbons were also simulated: CH, C_2H_2 with both hydrogen atoms bonded to a single carbon atom, and C_4H_4 (Figure 3.1). These small radical carbon and hydrocarbon molecules are expected to be present in various reactive gas manufacturing processes, if only transiently.
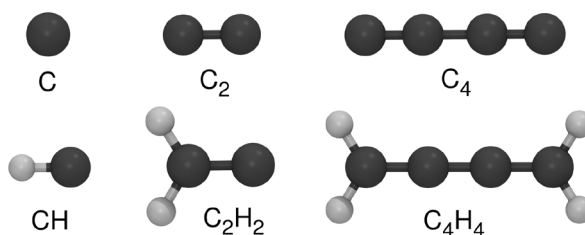

Figure 3.1 Initial gas molecules simulated.[1]

Two ReaxFF parameter sets were used to model the reactions. The parameter set of Nielson et al.[45] (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.[46] (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.

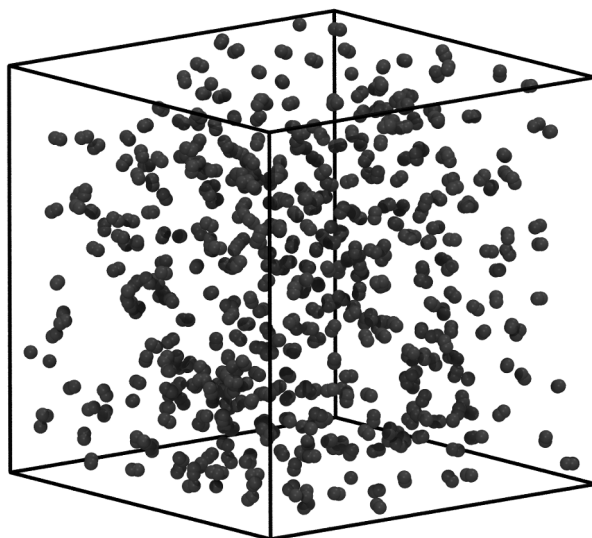Figure 3.2 Equilibrated system of C_2 molecules at 300 K.[1]

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^3 for the pure carbon systems and 0.02663 g/cm^3 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 Walls 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[86] software, which includes an implementation of the ReaxFF code. An example of an equilibrated system is shown in Figure 3.2.

Chapter 4: Results and Discussion

4.1 Time Step Size

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[32] 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_2 and acetylene molecules, as shown in Figure 4.1 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.
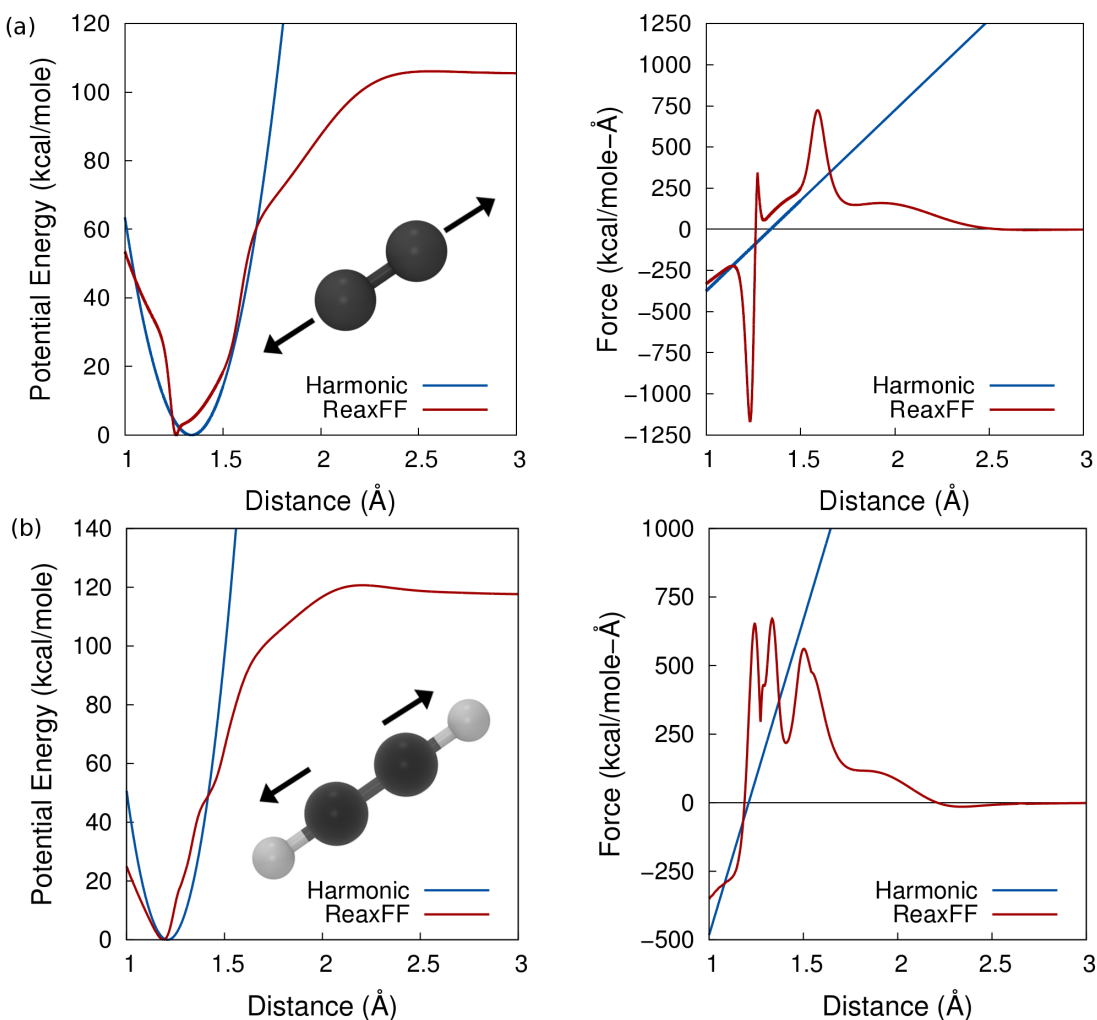
Figure 4.1 Comparison of the potential energy and force gradient between the ReaxFF and a generic harmonic potential for (a) a C_2 molecule (with a harmonic force constant of 549 kcal/mole and an equilibrium bond distance of 1.34 Å) and (b) acetylene (with a harmonic force constant of 1150 kcal/mol and equilibrium bond distance of 1.21 Å).[1]

An example of the influence of time step size on the simulated evolution of the reactive carbon gases is shown in Figure 4.2. 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

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of temperatures and initial gas molecules, the corresponding maximum time step sizes are listed in Table 4.1 and Table 4.2 for the Chenoweth and Nielson parameter sets, respectively.
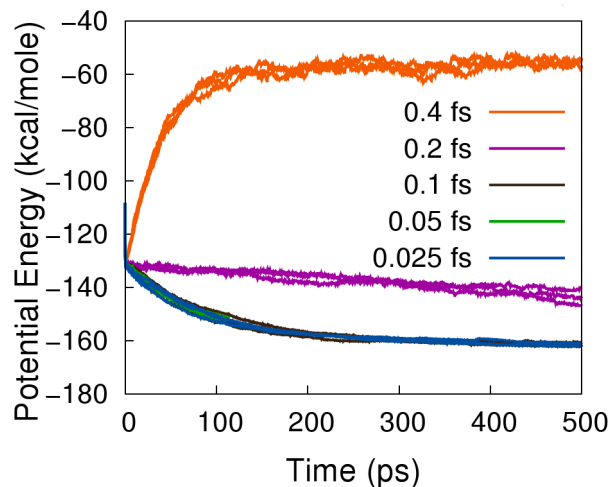

Figure 4.2 Influence of time step on potential energy convergence for a system of C_4 initial gas molecules at 1,500 K using the Chenoweth parameter set.[1]

Table 4.1 Maximum time step size for various reactive carbon gases at different temperatures using the Chenoweth parameter set.

Molecule	300K	1,500 K	3,000 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 4.2 Maximum time step size for various reactive carbon gases at different temperatures using the Nielson parameter set.

Molecule	300K	1,500 K	3,000 K
C	0.1	0.1	0.05
C2	0.1	0.1	0.05
C4	0.1	0.1	0.05
CH	0.2	0.1	0.1
C2H2	0.2	0.1	0.1
C4H4	0.2	0.1	0.1

The data in Table 4.1 and Table 4.2 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 Table 4.1 and Table 4.2 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.
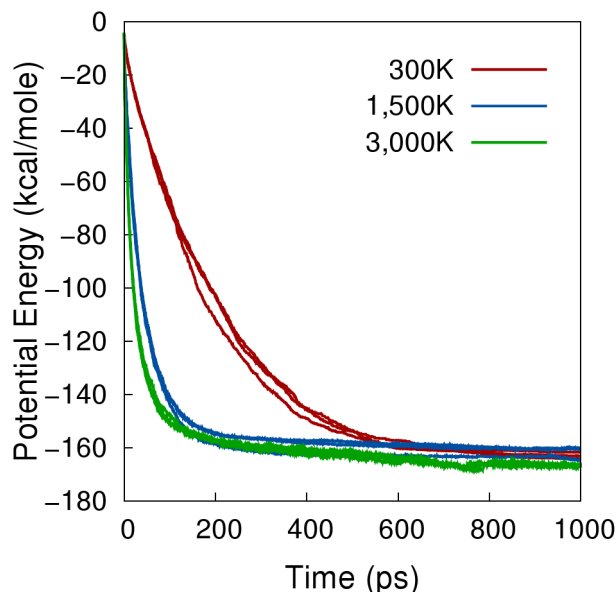
4.2 Temperature

Figure 4.3 Influence of temperature on potential energy convergence for an initial gas of C atoms using the Nielson parameter set.[1]

Figure 4.3 shows a typical plot of the influence of simulation temperature on the evolution of carbon reactive gases. The 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 4.4). 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 4.4).
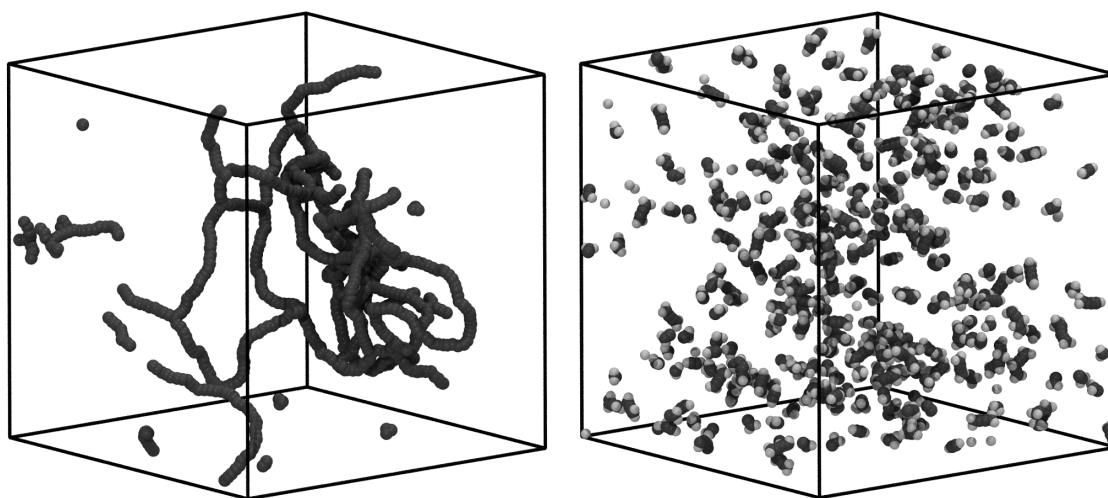

Figure 4.4 Final structures for initial gas of carbon atoms at 3,000 K with the Nielson parameter set (left) and an initial gas system of C_2H_2 at 3,000 K with the Chenoweth parameter set (right).[1]

4.3 Parameter set

Figure 4.5 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 4.5, 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.
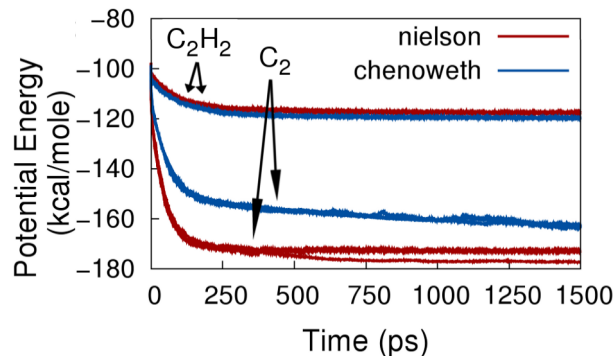
Figure 4.5 Influence of parameter set on potential energy convergence for initial gas of C_2 and C_2H_2 molecules at 1,500 K.[1]

4.4 Initial gas molecule

Figure 4.6 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 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.
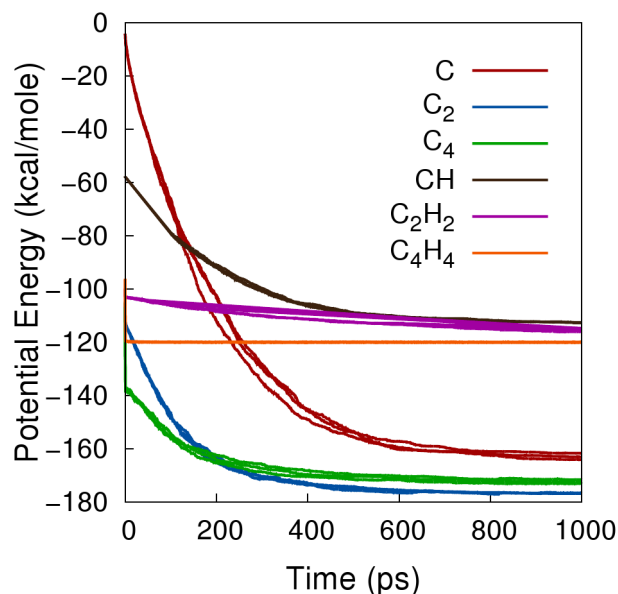
Figure 4.6 Influence of initial gas molecules on potential energy convergence, using the Nielson parameter set at 300 K.[1]

It is interesting to note that, for the Chenoweth parameter set at 3,000 K for all of the pure carbon systems, a structural transformation was observed at ~250 ps, as shown in Figure 4.7. 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.[87-89]
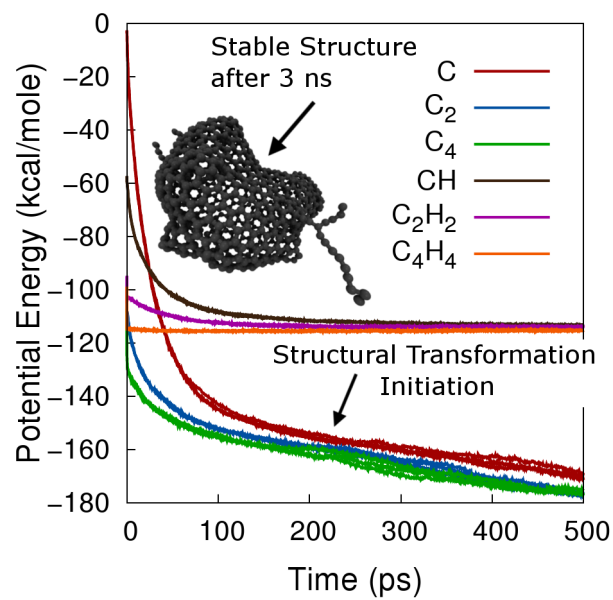
Figure 4.7 Structural transformation predicted in pure carbon systems, as indicated by a sudden decrease in the potential energy near 250 ps.[1]

Chapter 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 3,000 K, a time step of 0.05 fs should be used, whereas for lower temperatures (300 and 1,500 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.

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Appendix A: LAMMPS input script for acetylene dissociation curve

```
#--------initialization---------
units       real
dimension   3
boundary    f f f
atom_style  charge
atom_modify map hash
read_data   acetylene.charge
group       C1 id 1
group       C2 id 2
group       hydrogens subtract all C1 C2

#--------force-field------------
pair_style  reax/c NULL
pair_coeff  * * ffield.reax.chenoweth C C H
fix         chargeeq all qeq/reax 1 0.0 10.0 1.0e-6 reax/c
compute     reax all pair reax/c
variable    eb   equal c_reax[1]/count(all)
variable    ea   equal c_reax[2]/count(all)
variable    elp  equal c_reax[3]/count(all)
variable    emol equal c_reax[4]/count(all)
variable    ev   equal c_reax[5]/count(all)
variable    epen equal c_reax[6]/count(all)
variable    ecoa equal c_reax[7]/count(all)
variable    ehb  equal c_reax[8]/count(all)
variable    et   equal c_reax[9]/count(all)
variable    eco  equal c_reax[10]/count(all)
variable    ew   equal c_reax[11]/count(all)
variable    ep   equal c_reax[12]/count(all)
variable    efi  equal c_reax[13]/count(all)
variable    eqeq equal c_reax[14]/count(all)

#------harmonic bond equations------
variable    dist equal z[2]-z[1]
variable    reax_Cf equal fz[1]
```

```
compute       ppm C2 pe/atom
compute       ptm all reduce sum c_ppm
variable      reax_Ce equal c_ptm/count(C2)

#parameters from TINKER OPLS files
variable      b_CZe equal 1150.00*(v_dist-1.2100)^2
variable      b_CMe equal 549.00*(v_dist-1.3400)^2
variable      b_CZf equal 2*1150.00*(v_dist-1.2100)
variable      b_CMf equal 2*549.00*(v_dist-1.3400)


#-----------settings------------
timestep      0.5
thermo        100
thermo_style  custom step v_dist ke pe v_reax_Cf v_reax_Ce
thermo_modify norm yes


#----------minimize----------
fix           2 all viscous 0.3
min_style     cg
min_modify    line quadratic
fix           1 hydrogens nve
velocity      all set 0.0 0.0 0.0 units box
fix           freeze1 C2 setforce 0.0 0.0 0.0
fix           freeze2 C1 setforce 0.0 0.0 0.0
minimize      0.0 1.0e-6 10000 100000
unfix         freeze1
unfix         freeze2
run           400000
reset_timestep  0


#---Loop----------------------------------------
#------------------------------------------------
dump          1 all atom 16000 acetylene.lammpstrj
dump_modify   1 scale no
fix data all ave/time 1 1 8000 v_dist v_b_CZe v_b_CZf &
    v_b_CMe v_b_CMf v_reax_Cf v_reax_Ce file thermo.txt
variable      a loop 1 1500
label         loop


#-----------run------------
fix           1 C2 nve
```

```
velocity     C2 set 0.0 0.0 0.003 units box
fix          freeze all setforce 0.0 0.0 0.0
run          1
unfix        freeze


#----------minimize---------
unfix        1
fix          1 hydrogens nve
velocity     all set 0.0 0.0 0.0 units box
run          7999


#-------------------------------------------
#-----Loop End------------------------------
next         a
jump         in.script loop
```

Appendix B: Representative LAMMPS input script for a reacting gas

Input script for C_2 at 3,000 K using ReaxFF with Chenoweth parameters

```
#LAMMPS input file
log C2_3000K_chenoweth_0.025.log.lammps

#---------initialization---------
units       real
dimension   3
boundary    p p p
atom_style  charge
read_data   C2_3000K.charge

#--------force-field-----------
pair_style  reax/c NULL
pair_coeff  * * ffield.reax.chenoweth C
fix chargeeq all qeq/reax 1 0.0 10.0 1.0e-6 reax/c

#--------reax energies-----------
compute     reax all pair reax/c
variable    eb   equal c_reax[1]
variable    ea   equal c_reax[2]
variable    elp  equal c_reax[3]
variable    emol equal c_reax[4]
variable    ev   equal c_reax[5]
variable    epen equal c_reax[6]
variable    ecoa equal c_reax[7]
variable    ehb  equal c_reax[8]
variable    et   equal c_reax[9]
variable    eco  equal c_reax[10]
variable    ew   equal c_reax[11]
variable    ep   equal c_reax[12]
variable    efi  equal c_reax[13]
variable    eqeq equal c_reax[14]
```

```
#-----------settings------------
compute         ppa all pe/atom

timestep        0.025
variable        Time equal step*dt/1000 #time in picoseconds
thermo_style    custom step v_Time temp press etotal ke pe fmax
thermo_modify   norm yes flush yes

fix             integrate all nve
fix             thermostat all temp/berendsen 3000 3000 5
fix             momentum all momentum 2000 linear 1 1 1 angular

#---------minimize---------
min_style       sd
minimize        1.0e-4 1.0e-6 100 1000
reset_timestep  0

#------------run------------
thermo          20000 # 500 fs
variable        a loop 1 5 # 500 ps total

label           loop
Fix reaxdata all ave/time 40000 1 40000 v_Time v_eb v_ea v_elp &
     v_ev v_epen v_ecoa v_ehb v_et v_eco v_ew v_ep v_eqeq &
     off 1 file C2_3000K_chenoweth_0.025.reax$a.txt
Dump 1 all custom 40000 C2_3000K_chenoweth_0.025_$a.lammpstrj &
                                   id type x y z c_ppa

dump_modify  1 flush yes

run             4000000 #100 pecoseconds
write_restart   $a.restart
undump          1
unfix           reaxdata
next            a
jump            in.script1 loop
```

Appendix C: Copyright Permission