Reactive Molecular Dynamics Analysis of Spacecraft Monopropellants

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INTRODUCTION

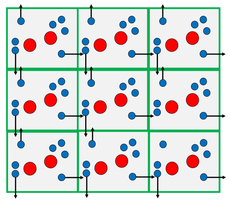
In order to simulate the reaction and consequently observe the evolution of individual species in a reaction, a computational tool known as Reactive Force-Field, or ReaxFF, is utilized. ReaxFF bridges the gap between quantum mechanical calculations, which can be very computationally expensive when considering phenomena at the electronic level, and classical calculations, which often make assumptions that do not give enough detailed information regarding the reaction mechanism. In this way, ReaxFF uses a bond order formalism based on the interatomic potentials as well as non-reactive atomic interactions. When ReaxFF is given initial and equilibrium conditions, the system's energy as a function of atom positions is produced[1]. The interatomic potentials are determined empirically. Since it is partly dependent on experimental evidence, reaction force fields can be "trained" by incorporating experimental results to improve the parameters originally set for the reaction.

ABSTRACT

In order to study the catalytic decomposition and ignition of various energetic liquids, reactive molecular dynamics simulations have been performed using ReaxFF. In addition to hydrazine, the most widely-used fuel for in-space propulsion, certain ionic liquid fuels are investigated. For each liquid, decomposition is simulated over a number of different platinum surfaces relevant to a real catalyst, beginning with idealized low-index surfaces and extending to vicinal surfaces and surfaces with regular defects, including step edges, kinks, and vacancies. In each of the idealized and low-coordination surface site simulations, the adsorption, decomposition, and desorption processes are observed and compared to *ab initio* calculations. Additionally, possible reaction pathways are tracked as they are encountered, with a fragment analysis to identify intermediate species. These simulations show that ReaxFF can be a valuable method for elucidating the reaction mechanisms of liquid catalytic decomposition without the need for trial-and- error or chemical intuition typically needed in an exclusively *ab initio* approach.

OBJECTIVES

- Create a simulation of hydrazine that replicates empirical data by implementing a reaction force field methodology
- Analyze trajectory file data (atom positions, bonds, bond orders, etc.) by determining existing individual molecules over various time-steps
- Post-process simulation results of a minimized system with a periodic boundary condition and track molecules of interest
- Implement similar methodology for thermal decomposition of ionic liquids and catalytic decomposition over Iridium catalysis

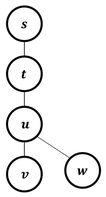


A periodic boundary condition assumes atoms interact in an infinite-boundary box. By the minimum image convention, each individual particle interacts with the closest image of the remaining particles in the system.

METHODS

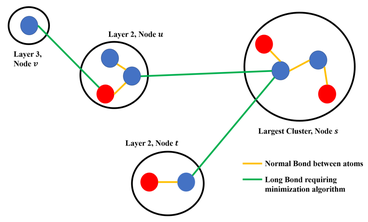
Depth-First Search Algorithm:

- Path from parent node *s* to child node *v* was directly searched first to find "deepest" node in path
- Unexplored neighboring nodes were recursively found (e.g. node *w*)
- Nodes (circles) represent atoms; edges (solid lines) represent bonds.



Breadth-First Search Minimization Algorithm:

- Neighbors were explored outwards from *s* in all directions, thus adding a layer of nodes at a time
- Used to identify "clusters" of atoms separated by bonds with length longer than half the boundary box

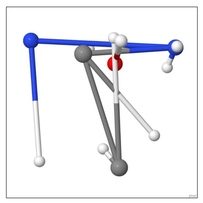


Molecule Tracking Algorithm:

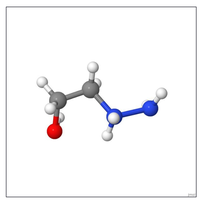
- Between timesteps, atoms and molecules were assigned unique identification numbers
- History trees of specified atom ID's were determined and post-processed to investigate potential species of the reaction mechanism

RESULTS

Before Minimization Algorithm



After Minimization Algorithm



Hydrazine Decomposition Initialized to 298 K

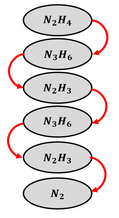
Predicted Reaction Mechanism[2]

1. Initiation:	$\mathbf{X^* + N_2H_4 \rightarrow X + 2NH_2}$
2. Propagation:	$\mathbf{N_2H_4 + NH_2 \rightarrow N_2H_3 + NH_3}$
	$\mathbf{N_2H_3 + X \rightarrow N_2 + H_2 + H + X^*}$
	$\mathbf{H + N_2H_4 \rightarrow NH_3 + NH_2}$
3. Branching:	$\mathbf{N_2H_3 + X \rightarrow NH + NH_2 + X}$
	$\mathbf{N_2H_4 + NH \rightarrow NH_2 + N_2H_3}$

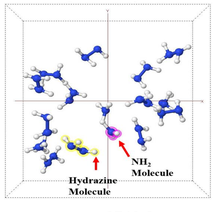
Implementation of Molecule Tracking Algorithm

Timestep (fs)
8300
8340
8480
8760
8830
9320

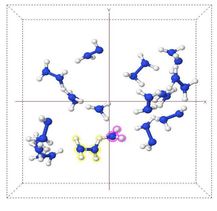
Tracking Nitrogen Atom No. 104:



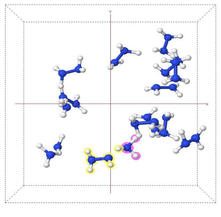
$t_1 = 8300\ fs$



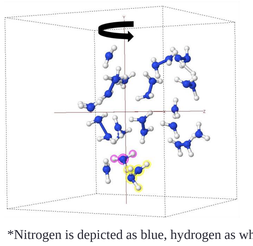
$t_2 = 8340\ fs$



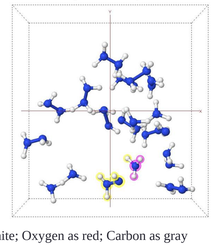
$t_3 = 8480\ fs$



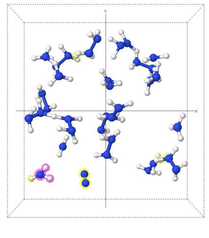
$t_4 = 8760\ fs$



$t_5 = 8830\ fs$



$t_6 = 9320\ fs$



*Nitrogen is depicted as blue, hydrogen as white; Oxygen as red; Carbon as gray

DISCUSSION

Minimum Image Convention

- As atoms cross over box boundary between time steps, minimization algorithm corrects for periodic boundary condition to show the true molecule structure of the $C_2H_9N_2O$ test case
- Use of clusters ensures large molecules spread across boundary planes are correctly minimized

Molecule Tracking of Hydrazine Molecule

- During first time step of initialized decomposition reaction at t_1, hydrazine and amino radical, $N_2H_4 + NH_2$, are present
- Within 40 femtoseconds, product of first propagation step is identified as the transition state N_3H_6
- After 140 fs, equilibrium products $N_2H_3 + NH_3$ match expected propagation products; between t_4 and t_5, transition state is revisited before returning to propagation products
- At t_6, hydrogen atom dissociates, thus producing more NH_3 and N_2, signifying the occurrence of the second propagation reaction

FUTURE WORK

Ionic liquids, otherwise known as "green" monopropellants, pose increased thrust performance per mass density and less toxicity compared to hydrazine, thus providing a significant cost advantage as it applies to spacecraft propulsion. However, the thermal and catalytic decomposition reaction mechanisms for such fuels are undetermined. By implementing a reactive force field to predict quantum chemical interactions, resulting data will be analyzed using minimization and molecule tracking algorithms.

REFERENCES

[1]Senftle, Thomas P, et al. "The ReaxFF Reactive Force-Field : Development, Applications and Future Directions." NPJ COMPUTATIONAL MATERIALS, 2016, pp. NPJ COMPUTATIONAL MATERIALS, 2016.

[2]Schmidt, E. *Hydrazine and Its Derivatives: Preparation, Properties and Applications;* Wiley: New York, 1984