

Molecular Dynamics of Reactive Plasmas

Introduction and Motivation

In response to climate change and the effects of greenhouse gas emissions, there is an international push to decarbonize and electrify the chemicals industry¹. Plasma reactors and plasma-catalytic reactors are two of the many approaches being investigated to aid in this push². These reactors get energy from electricity instead of from a thermal source, which would normally be the combustion of fossil fuels. The plasma science community is fairly well established, with many applications in various industries ranging from pollution control to material synthesis². Because of the relative novelty of plasma-catalytic reactors, however, some fundamental reactor-design principles are not well established. These principles include accurate thermodynamic frameworks, energy efficiency limits, and detailed kinetic models³.

One of the main hurdles for kinetic models of plasma-catalytic systems is the interactions between plasma species and the catalytic surface. When we consider plasma species in nonthermal, or low temperature, plasmas, we mean gas molecules that have been excited by the super-heated electrons within the plasma phase. These excitations are generally vibrational excitations, translational excitations, rotational excitations, or sometimes electronic excitations. Additionally, some ionized species are present and collide with the surface. Because of the high-energy nature of the species colliding with the surface, a lot of exciting chemistry takes place, which is the reason plasma-catalysis is used. However, it also makes the modeling of these interactions difficult. For example, traditional Molecular Dynamic (MD) simulations using classical-mechanics force fields do not usually allow for electronic excitations or charged particles. Other simulation techniques that use quantum-mechanics based physics, such as Density Functional Theory (DFT) calculations or ab-initio MD, would require immense computational expense to adequately capture the size or time-scale of these surface interactions.

Nonetheless, many clever approaches to atomistic simulation techniques for plasma-surface interactions are reported in the literature^{4,5,6,7,8}. MD is the preferred technique in the literature, simply for its ability to capture longer time scales and larger systems than other techniques. Although, some stochastic Monte Carlo (MC) methods are also employed. The general approach is to use force fields that allow for reactions; thus, the individual charges can be taken into account. However, many approaches exist that take into account any number of various effects that come about because of the plasma-surface chemistry.

Another general issue for thermodynamic and kinetic modeling of plasma-catalytic systems is capturing the bounteous chemistry present in the plasma phase. The presence of super-energetic electrons, radicals, and ions in this phase leads to difficulty in modeling such a system using classical mechanics. Part of this issue is due to the charges, but that is readily solved with simple force field parameterization. The bigger hurdle is allowing for bonds to break, for reactions to happen, and for excitations to occur. Electronic excitations will not be captured by classical mechanics, so we will not worry about those in this work, but the reactivity of a system can and has been captured using specially-designed force fields.

For this work, I will be exploring some of the results of Somers et al.⁹ that they got using an MD force field developed for hydrocarbon-nickel reactions. This force field is called ReaxFF, and was developed by Mueller et al.¹⁰. Somers et al. have produced results that are explicitly related to hydrocarbon plasma-catalytic chemistry; this is not only an early example of plasma-catalytic surface modeling, but is also closely related to a larger ethane dehydrogenation project that I am working on. I will also show how using the ReaxFF force field to model gas-phase reactions, and how it may be applied to plasma-catalytic systems.

Methods

I first explored the work of Somers et al.⁹, who investigated the interactions between a Nickel FCC (111) surface and methane radicals coming from a nonthermal plasma. I would have used the LAMMPS software package to do the simulation myself, but it does not currently support this particular form of the ReaxFF force field. Other software packages, such as the commercially licensable Amsterdam Modeling Suite (SCM), does support this model, but due to the budget and time constraints of this project, I will simply report on the results of Somers et al. There are many computational inputs required for an MD simulation, many of which were expressly mentioned by Somers et al. Those mentioned are summarized in Table 1. Nearly all of these inputs have been explained in my Molecular Modeling and Simulations class, which allowed me to be able to understand and apply their results to this project.

Table 1. MD Inputs From Somers et al. (2012)

Input Description	Value	Units	Note
Number of Nickel atoms	300	-	
Number of Nickel (111) layers	6	-	
Boundary conditions (x,y)	Periodic	-	
Equilibration Temperature	400	K	
Equilibration Thermostat	Berendsen thermostat	-	
Equilibration coupling constant	100	fs	
Relaxation ensemble	NVE	-	
Plasma species z position	5	Å	Above the top layer of Nickel surface
Plasma species (x,y) position	Random	-	
Plasma species initial velocity vector	Random	(x,y,z) direction	

Plasma species initial velocity magnitude	2.494E-4	Å/fs	RMS velocity of methane at 400K
Time following impact	4	ps	In the NVE ensemble
Number of repeats of non-consecutive impacts	500	-	
Time following impact for consecutive collisions	5	ps	
Number of repeats of consecutive impact experiments	5	-	This is the number of times the simulation is performed, not the number of impacts

Somers et al. explained that they used the ReaxFF force-field for their simulations. I was not able to find the force field from their paper, but did find the original paper, which has the force field parameters for a Nickel, Carbon, Hydrogen system¹⁰. While LAMMPS supports a limited number of ReaxFF force fields, this is not one of them. Nonetheless, it can be found in this project's github repository (see Reproducibility section for link).

The results of these impacts are three possible outcomes for each impact: the plasma species adsorbs, reflects, or decomposes. The outcomes are recorded, and statistical analysis gives a reasonable insight into what really occurs when the radical impacts the surface.

As one may gather from Tables 1, the model begins by simulating a periodically repeating, 6-layer thick Nickel surface (FCC (111), (100), or one of two step-edge surfaces). The surface has a vacuum above it, and is brought to equilibrium in a Berendsen thermostat at 400 K. It is then relaxed in the NVE ensemble. A plasma species (in this case a methane radical) is placed about 5 Å from the top of the surface. The simulation ran by giving the plasma species a randomly oriented velocity, which had the magnitude of the RMS velocity based on the surface's temperature. This species impacted the surface, and the simulation tracked the movement and bonds formed for both the plasma species and the Nickel surface for 4 ps following the impact. In a separate set of simulations, they also studied consecutive impacts. In these cases, after the original impact, the system is followed in the NVE ensemble for 5 ps, then equilibrated to 400 K. At that point, the equilibrated system is hit again with a radical (with a new randomized velocity vector), and the process repeats itself. This is repeated until clear trends become apparent.

For the second part of this project, I used an example ReaxFF force field script in the LAMMPS database to simulate gas-phase hydrocarbon chemistry. This example script is very simple, containing only 105 atoms in box with 2.5 nm on each side, beginning at 0 K, running for 5000 ps. To see how the ReaxFF captures more realistic chemistry I updated the code to begin at 800 K, and by giving the atoms random starting velocities. The LAMMPS input and output files are on the github repo mentioned in the Resources section.

Similar to the surface-radical interaction simulation, this hydrocarbon oxidation simulation begins with an equilibration in the NVE ensemble, then a reaction using the ReaxFF inputs, then an equilibration using the Berendsen thermostat with a 100 fs coupling constant. Unlike the surface-radical interaction, all of the molecules are moving in this simulation. This is because the focus is on the gas phase chemistry, and there is no surface involved.

Results and Discussion

The trajectories of the methane radicals modeled by Somers et al. were followed and analyzed for three possible outcomes (adsorption, reflection, decomposition). Interestingly, the adsorption probability did not depend strongly on surface facet, but the decomposition probability did. For both adsorption and decomposition, the type of radical had the largest impact on probability; the three types tested were CH_3 , CH_2 , and CH . Somers et al. provide a more detailed description of their results, but their figure summarizing the single-impact results is included below.

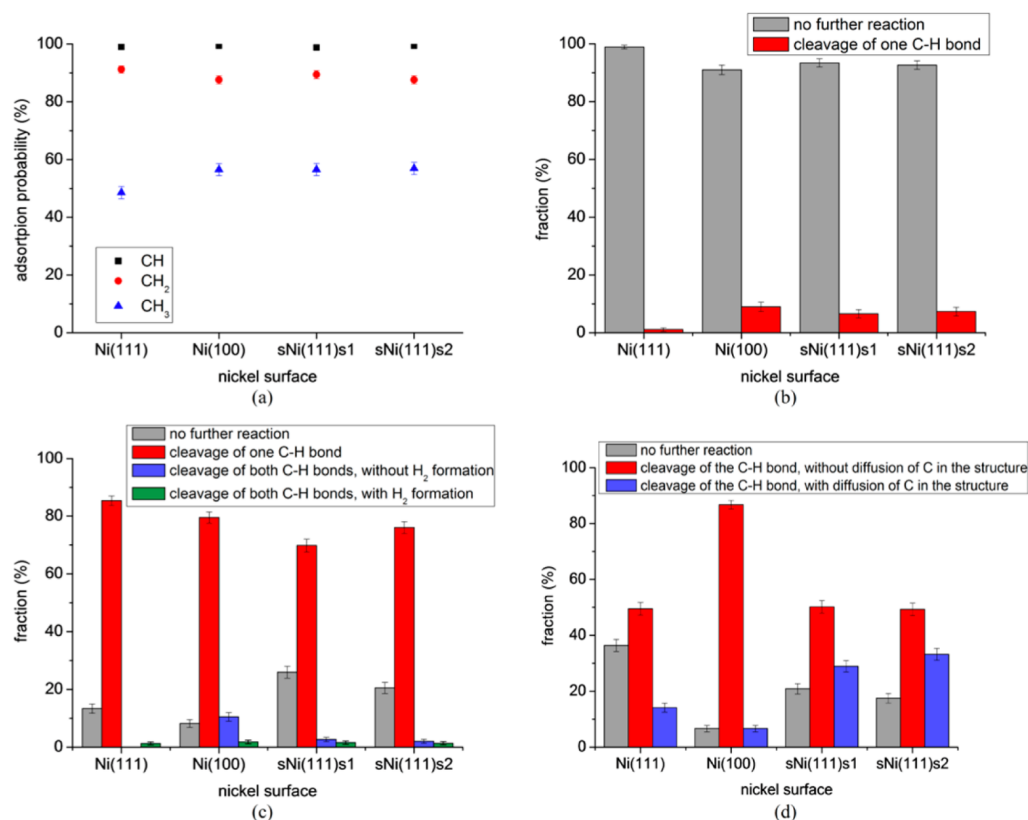
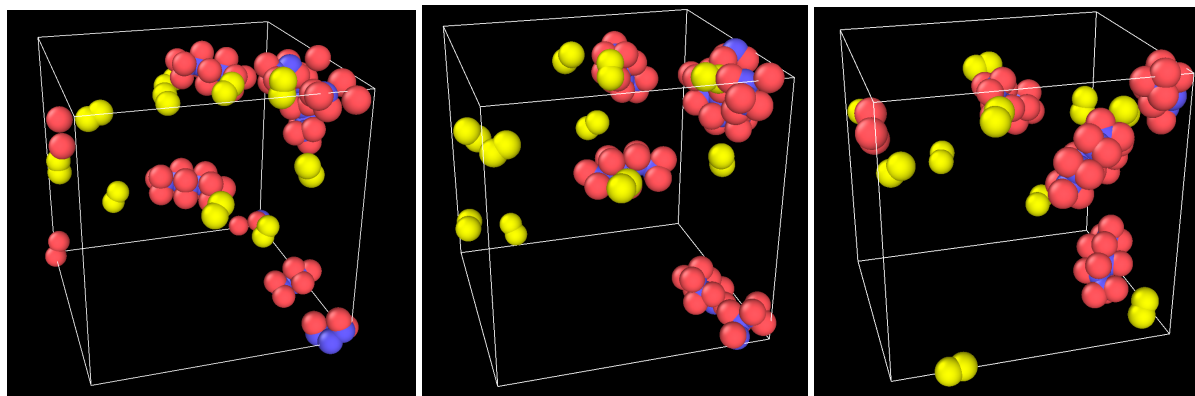


Figure 2. (a) adsorption probabilities and associated standard deviations for the single impacts of the CH_x radicals on the four different nickel surfaces. (b), (c), and (d) observed reactions and the associated standard deviations after adsorption of respectively CH_3 , CH_2 , and CH .

The hydrocarbon oxidation simulation provides us with an interesting snapshot into the dynamics of gas-phase reactions. The simulation box is shown in the figure below, with left to right being temporal progression. It is a fairly sparse box, but the simulation shows the influence of the reactive force field on the movement of the atoms. In these conditions, the hydrocarbons actually tend to clump.



Applying this type of force field to a plasma-phase system is not necessarily straightforward, as the force field would need to be calibrated to the charged and excited particles. However, the ability to do so would be a powerful tool in developing kinetic models, because of the ability to elicit rate constants.

Conclusions

The use of MD simulations for plasma-catalytic systems has the advantage of time- and size-scales appropriate to model the reactive interactions present. This does, however, require the use of specialized force fields that allow for bond breakage and formation, for charged particles, and for multiple phases (solid and gas/plasma). One force field type that has been developed to accommodate for these things is the ReaxFF force fields. Somers et al. showed they can be readily applied to modeling plasma-catalytic systems. While I would have gladly repeated these calculations, their results are promising for future endeavors. Of particular interest is using their successful force fields to model larger hydrocarbons (such as ethane and ethane radicals) using SCM or an altered approach in LAMMPS.

Results from a simple gas-phase MD simulation using the ReaxFF force field show that these force fields are able to capture gas-phase chemistry in addition to molecular motion and forces. Thus, they can also be readily applied to more complex plasma-phase systems, in which hydrocarbons such as light alkanes are activated. Ideally, I will be able to couple both the plasma phase and surface interactions in a full-system model. This could be a major step forward in modeling these systems, and in understanding the complex yet exciting chemistry of plasma-catalysis.

Reproducibility

Resources are found at https://github.com/djhaycock/MMS_FinalProject.

References

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