

REACTIVE FORCE FIELDS BASED ON QUANTUM MECHANICS FOR APPLICATIONS TO MATERIALS AT EXTREME CONDITIONS

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Abstract: Understanding the response of energetic materials (EM) to thermal or shock loading at the atomistic level demands a highly accurate description of the reaction dynamics of multimillion-atom systems to capture the complex chemical and mechanical behavior involved: nonequilibrium energy/mass transfer, molecule excitation and decomposition under high strain/heat rates, formation of defects, plastic flow, and phase transitions.

To enable such simulations, we developed the ReaxFF reactive force fields based on quantum mechanics (QM) calculations of reactants, products, high-energy intermediates and transition states, but using functional forms suitable for large-scale molecular dynamics simulations of chemical reactions under extreme conditions.

The elements of ReaxFF are:

- charge distributions change instantaneously as atomic coordinates change,
- all valence interactions use bond orders derived uniquely from the bond distances which in turn describe uniquely the energies and forces,
- three body (angle) and four body (torsion and inversion) terms are allowed but not required,
- a general “van der Waals” term describes short range Pauli repulsion and long range dispersion interactions, which with Coulomb terms are included between all pairs of atoms (no bond or angle exclusions),
- no environmental distinctions are made of atoms involving the same element; thus every carbon has the same parameters whether in diamond, graphite, benzene, porphyrin, allyl radical, HMX or TATP.

ReaxFF uses the same functional form and parameters for reactive simulations in hydrocarbons, polymers, metal oxides, and metal alloys, allowing mixtures of all these systems into one simulation.

We will present an overview of recent progress in ReaxFF developments, including the extension of ReaxFF to nitramine-based (nitromethane, HMX) and peroxide-based (TATP) explosives. To demonstrate the versatility and transferability of ReaxFF, we also present applications to silicone polymer poly-dimethylsiloxane (PDMS).

Keywords: reactive force field, molecular dynamics, detonation, energetic materials, nitromethane, polymers

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INTRODUCTION

The atomistic mechanisms of the fundamental chemistry and physics of condensed-phase materials under extreme conditions that experimentally may be challenging to investigate (e.g. ultrafast laser heating, propellant combustion, shock compression, and detonation) are still not well understood. Quantum mechanics (QM) can provide a reliable description of the above processes with a valuable insight into the energy barriers and reaction pathways. However, QM methods are still practical only for systems too

small to describe coupling of chemical and mechanical behavior at the requisite level of spatiotemporal resolution (e.g. for simulation of voids, dislocations, grain boundaries, and interfaces).

Recently, we developed the ReaxFF force field in order to describe chemical reactions in classical molecular dynamics (MD) simulations that are many orders of magnitude faster than the QM methods. We have found that ReaxFF can reproduce QM-energies for reactive systems, including reactants, transition states and products, for a wide range of materials, such as hydrocarbons,¹ nitramines,^{2,3} silicon/silicon oxides,^{4,7} aluminum/ aluminum oxides,⁸ transition

metal interactions with first-row elements,⁹ and magnesium/ magnesium hydrides.¹⁰ This allows dynamic simulations of materials under a wide range of heat or shock loading conditions, including initiation and detonation of solid EM and EM composites. The ReaxFF functional form is suitable for highly scalable parallel MD codes, making possible MD simulations of chemical reactions in systems with millions of atoms.¹¹

METHODOLOGY

ReaxFF employs instantaneous bond orders (BO_{ij}), including contributions from sigma, pi and double-pi bonds, which are calculated from the interatomic distances (r_{ij}); these instantaneous bond orders are subsequently corrected with overcoordination and undercoordination terms to force systems towards the proper valency. These bond orders are updated every MD-iteration, thus allowing ReaxFF to recognize new bonds and to break existing bonds.

ReaxFF partitions the overall system energy into contributions from various partial energy terms. These partial energies include bond-order dependent terms like bond energies, valence angle, lone pair, conjugation, and torsion angle terms to properly handle the nature of preferred configurations of atomic and resulting molecular orbitals, and bond-order independent terms that handle non-bonded van der Waals and Coulomb interactions. These non-bonded interactions are calculated between *every* atom pair, irrespective of connectivity, and are shielded to avoid excessive repulsion at short distances. In addition, the charges of the atoms depend continuously on the geometry using general expressions based on atom electronegativity and hardness, whose parameters are also derived from QM. This treatment of non-bonded interactions allows ReaxFF to describe covalent, ionic, and intermediate materials with the same parameters, thus greatly enhancing its transferability. For a more detailed description of these partial energy terms, see Ref. [1,9].

APPLICATIONS

We have compared the ReaxFF results on extreme chemistry at high temperatures to QM-

based dynamic simulations and experiments.³ Our ReaxFF simulations of constant-temperature (NVT) thermal decomposition of HMX crystal performed at the same conditions used in QM-DFTB simulations ($T\sim 3500\text{K}$, $V/V_0\sim 0.80$),¹² display a reasonable agreement in final product distributions (Fig. 1).

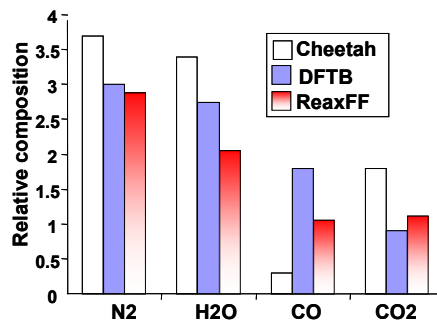


Figure 1. Dominant species in thermal decomposition of HMX obtained both from ReaxFF and DFTB MD simulations and Cheetah thermochemical calculations.

Likewise, the recent ReaxFF results on thermal decomposition of condensed-phase nitromethane¹³ ($T=2000\text{--}4000\text{K}$, $V/V_0=0.6$) agree well with DFT-MD¹⁴ and CPMD¹⁵ simulations both for constitutive parameters such as the pressure evolution during the decomposition from 25 GPa to 35 GPa (see Fig.2), and the initial chemical events such as intra-molecular proton transfer responsible for a formation of CH_2NO_2 and CH_3NOOH intermediates. In particular, we performed NVT simulations with ReaxFF in liquid and solid nitromethane at high temperatures (2000-4000 K) and density 1.97 g/cm^3 for times up to 200 ps. At $T=3000\text{ K}$ the first reaction in the decomposition of nitromethane was an intermolecular proton transfer leading to CH_3NOOH and CH_2NO_2 . For lower temperatures ($T=2500$ and 2000 K), the first reaction was often an isomerization reaction involving the scission of the C-N bond and the subsequent formation of a C-O bond to form methyl nitrite CH_3ONO . Also at very early times we observed intra-molecular proton transfer events. The main product of these reactions was H_2O , which began forming following the initiation steps. The appearance of H_2O marked the beginning of the exothermic chemistry. A good agreement between the ReaxFF-MD and DFT-based MD simulations¹⁴ on the pressure evolution during a fast annealing ($\sim 0.6\text{ ps}$) of compressed

nitromethane crystal (see Fig. 2) provides a direct validation of the ReaxFF at extreme conditions.

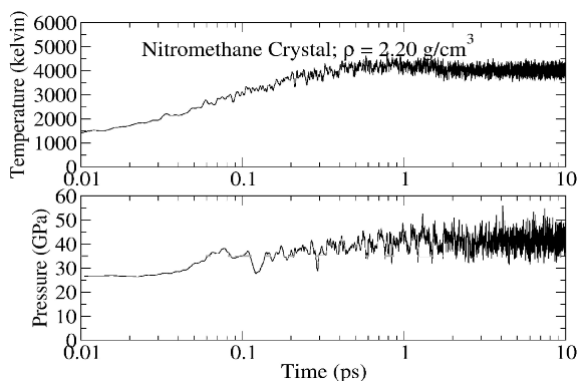


Figure 2. Temperature and pressure evolution during a fast annealing from 1000K to 4000K in the ReaxFF–MD simulations. Correspondingly, QM-based MD [14] lead to a pressure of 25 GPa at 1000K with an increase to 35 GPa after the heating to 4000K, in a good agreement with the ReaxFF results.

One of the most important features of the ReaxFF is a capability to describe chemical reactions in composite systems with a wide variety of constituents, including metals and polymers, with the same set of force field parameters. As an example, we study the poly-dimethylsiloxane (PDMS) – silicone polymer commonly used due to its superior thermal stability which makes it useful for a wide range of applications. The strength of PDMS can be improved through the addition of reinforcing filler such as silica particles. This silica-filled PDMS is used as cushioning and mechanical support in high temperature, high pressure environments. Therefore, it is important to understand the rapid decomposition processes that the polymer may undergo when exposed to extreme conditions. Using ReaxFF, we can gain insight into how the decomposition process is initiated and progresses by observing the changes in bonding associated with the degradation of PDMS as well the evolution of solid products (see Fig. 3). In order to study these processes for PDMS and PDMS exposed to various chemical environments, the silicon oxide ReaxFF force field⁴ was expanded to include silicon-carbon systems. From NVT-MD simulations using ReaxFF, we find that the initial thermal decomposition products of PDMS are the methyl radical and the associated polymer-radical, indicating that decomposition and

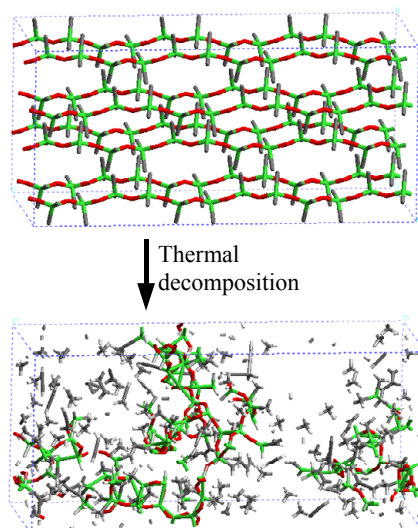


Figure 3: The thermal decomposition of PDMS in the ReaxFF NVT-MD simulation after 60 ps at $T=3500\text{K}$.

subsequent cross-linking of the polymer is initiated by Si-C bond cleavage.

Secondary reactions involving these methyl radicals lead primarily to formation of methane. We also studied the temperature and pressure dependence of PDMS decomposition by following the rate of production of methane in the ReaxFF MD-simulations. The Arrhenius-parameters for the failure modes of PDMS were determined by following the temperature-dependency of the methane production. Furthermore, we found that at increased pressures the rate of PDMS decomposition drops considerably, leading to the formation of fewer methyl radicals and methane molecules. Finally, we studied the influence of various chemical environments on the stability of PDMS. We found that the addition of water, nitrogen monoxide, or a SiO_2 -slab has no direct effect on the short-term stability of PDMS but addition of reactive species such as ozone leads to significantly lower PDMS decomposition temperature. The addition of nitrogen monoxide does retard the initial production of methane and C_2 hydrocarbons until the nitrogen monoxide is depleted. These results, and their good agreement with experimental data, demonstrate that ReaxFF provides a useful computational tool for studying the details of the rapid decomposition mechanism and the chemical stability of polymers⁷.

To study the initial chemical events related to the detonation of triacetoneperoxide (Fig. 4) commonly used in Improvised Explosive Devices (IED), we carried out molecular dynamics (MD) simulations using the ReaxFF reactive force field.¹⁶

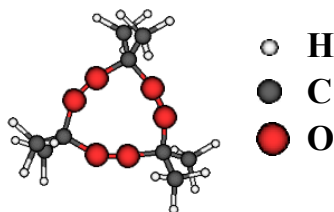


Figure 4: TATP molecular structure.

Our simulations demonstrate that thermal initiation of condensed phase TATP is entropy-driven (rather than enthalpy driven), since the initial reaction (leading mainly to the formation of acetone, O₂, and several unstable C₃H₆O₂-isomers) is almost energy-neutral. The O₂ generated in the initiation steps is subsequently utilized in exothermic secondary reactions, leading finally to formation of water and a wide range of small hydrocarbons, acids, aldehydes, ketones, ethers and alcohols (see Fig. 5).

All simulations and force field optimizations reported here used the ReaxFF-program,¹⁷ which carry out both MD-simulations and force field optimization using the ReaxFF energy description.

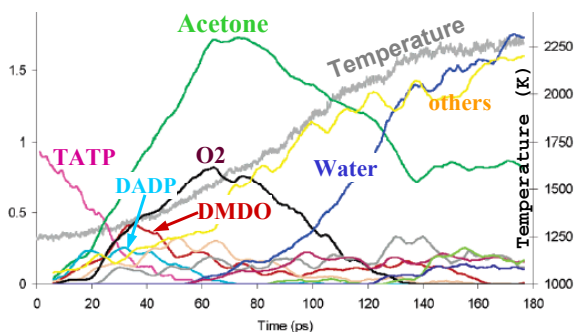


Figure 5: Product frequencies per TATP molecule found in NVE simulation of TATP decomposition after initial heat up at T=1250 K. Primary reaction products are acetone, oxygen, diacetonediperodix (DADP), and dimethyldioxacyclopropane (DMDO). All minor products are summed in “others”

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- The ReaxFF-program is available for distribution to academic users. For further information please contact ACTvD (duin@wag.caltech.edu) or WAG (wag@wag.caltech.edu).