



Observation of deflagration wave in energetic materials using reactive molecular dynamics



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ABSTRACT

Currently, there is no universal atomistic approach for simulating the combustion chemistry of a moving deflagration wave in condensed phase energetic materials. A reactive molecular dynamics based approach is used to identify the thermochemical events behind the formation and the propagation of a thermally initiated deflagration wave in the condensed phase RDX. The reactive molecular dynamics trajectory is mapped onto Eulerian control volumes to calculate the mass, energy and chemical flux across such deflagration front. A transition from ignition to a self-sustaining deflagration front occurs when the mass transport at the front exceeds the thermal transport in the course of propagation. Upon the formation of a self-sustaining deflagration front, a sudden rise in temperature at the front is observed accompanied by increase in the local density of the unreacted solid ahead of the front. The observed energy flux across the propagating deflagration front agrees well with the previously reported heat of explosion predictions. The deflagration front chemistry of RDX is dominated by the intermolecular and the intramolecular H-transfer reactions and subsequent formation of short-lived heavier polyradicals similar to the non-volatile residue reported in the literature. Chemical analysis indicates that the deflagration front is composed of a reactive chemical mixture of molten RDX, polyradicals and lighter intermediate radicals with intact triazine rings.

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1. Introduction

Safety and efficacy of propellants and energetic solids are determined by our understanding of reaction chemistry and transport at the combustion front. Self-sustaining combustion fronts may originate from a small reactive kernel or “hot spots” in solids. The hot spots need to meet certain criteria before forming a self-sustaining reaction front in the condensed phase. In the traditional terminology used by researchers such as Zeldovich [1], a self-sustaining reaction front can propagate through a system via different modes. For example, the reactive ignition front can lead to an instantaneous thermal explosion or can form a subsonic deflagration or a supersonic detonation front that consumes the remaining material. These different modes of the reaction front propagation were demonstrated in H₂-CO-air and H₂-air mixtures with and without hot spots by Gu et al. [2] using the continuum scale computations with detailed kinetic models for the chemical reactions. Among the reactive solids, the energetic materials (EM) are the most likely candidates for initiating a self-sustaining combustion wave. In condensed phase, various dissipative mechanisms such

as void collapse [3–5], viscous heating due to moving dislocations [6,7], shear band localization [8–11] and grain-grain friction [12,13] can create hot spots. In this article, we do not differentiate the hot spots by their origin. Instead, we focus on understanding the interplay between the chemistry and the propagation of deflagration fronts in the condensed phase. The theory of combustion fronts in solids is a particularly challenging problem. A highly non-linear nature of transport dynamics, unknown chemistry under high-pressure/temperature conditions and a lack of standardized kinetic models contribute to a simplified model for deflagration chemistry used in the energetics and propellants community.

In the traditional continuum theory based simulations, the combustion fronts in EM are traditionally treated using a two-phase model where the gas products are produced at the front while the consumption of the condensed phase energetic material is expressed using energy, mass and momentum conservation equations [14–16]. The *P-V-T* states of the gas-phase are calculated using a simplified equation of state (EOS) and the rest of the energetic material is treated as a non-reacting phase with constant heat capacity, thermal conductivity and other material properties such as sound speed. The energy due to the chemical reactions is expressed as a source term and is generally estimated using Arrhenius kinetics of a predefined reaction mechanism. The choice of a reaction mechanism varies considerably among different stud-

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ies. For example, a simple one-step reaction was used in the Euler equations of reactive flows to simulate the hot spot formation [17] and the shock to detonation transition [18] in HMX. Tarver et al. used a three-step chemical model in the heat transfer computer code TOPAZ for investigating the impact induced hot spots in solid explosives [19]. It needs to be pointed out that the chemical reactions and steps are not mechanisms with chemical basis. The one-step or three-step reactions in the reaction zone are models and the actual mechanism of the propagation of the reactions in condensed phase RDX is unknown. As a result, the chemistry models are subject to improvements as continuum simulations are able to handle the chemical complexity. For example, Rai and Udaykumar [5] used a more detailed Henson–Smilowitz [20] multi-step mechanism (10 chemical reactions) in the compressible Eulerian simulations to investigate the sensitivity of HMX towards its microstructure. For the steady state combustion of RDX at liquid–gas interface, Kumbhakarna et al. [21] used separate chemical mechanisms for the liquid RDX and the gas products. They described the thermal decomposition of liquid RDX into the gas products using two chemical reactions. The reactive chemistry of the high-temperature gas products was further modeled using a mechanism consisting of 504 chemical reactions. Besides the chemical dependence, some of these methods also depend on the phenomenological models such as the ignition and growth model [22], the Forest Fire model [23], the Johnson–Tang–Forest (JTF) model [24] and SURF model [25]. Such models describe the evolution of a hot spot as a function of mass fraction reacted and shock pressure. These phenomenological models require fitting of several empirical constants from the experiments for each specific configuration.

Recently, efforts were also made to include such Arrhenius reaction kinetics in the sub-continuum method of Dissipative Particle Dynamics (DPD). The DPD is a mesoscale particle-based method which uses a conservative force (inter-particle interaction), a dissipative force (friction, depends upon particle velocity) and a random force (white noise) to keep track of the positions and velocities (momentum) of all particles. Maillet et al. [26] used a Reactive DPD at constant energy to capture the shock to detonation transition in liquid nitromethane. They used a classical exp-6 potential for the inter-particle interactions (conservative force). A simple two-step mechanism ($\text{NiMe} \leftrightarrow \text{NiMe}^* \leftrightarrow \text{Products}$, NiMe represents nitromethane, NiMe* represents metastable intermediate state) was used to describe the chemistry of the thermal decomposition. Brennan et al. [27] developed a variant of reactive DPD model (named DPD-RX) for the non-equilibrium dynamics of heterogeneous materials. For studying the thermal decomposition of RDX, they initially parameterized the coarse-grain (CG) potentials for the inter-particle interactions. For describing the reaction chemistry, they used one unimolecular ($\text{RDX} \rightarrow \text{Gas products}$) and three bimolecular (gas products only) irreversible reactions. Although such continuum and sub-continuum modeling approaches served some engineering applications well, they still need a *a priori* knowledge of the reaction chemistry. This inherent dependence on the predefined chemistry limits their scope and the accuracy.

The reactive molecular dynamics (RMD) simulations which can capture chemical reactions on the fly can be used to fill this gap in our fundamental understanding of the molecular/atomistic physics and the chemistry of reactive flows under extreme conditions. The ReaxFF reactive force field [28–30] is one of the most widely used interatomic potentials for the RMD simulations. The force field parameters are parameterized against quantum calculations and can simulate complex chemical systems. The RMD simulations with ReaxFF has been previously used to study the combustion of coal [31] and nanoenergetic particles [32]. For energetic materials, it has been used to investigate the intermolecular energy transfer at a hot spot interface [33] and to investigate the ignition

and detonation chemistry of different propellants under mechanical [34–39] or thermal shocks [40]. RMD has also been used to study the shock-induced hot spot initiation due to shear localization at non-uniform interfaces containing RDX-HTPB (hydroxyl terminated polybutadiene) [41]. The authors found that the hot spot is more likely to form at RDX-HTPB interface due to shear localization which subsequently leads to detonation. Similar RMD simulations were performed for pentaerythritol tetranitrate (PETN) and silicon pentaerythritol tetranitrate (Si-PETN) [42]. However, due to the small simulation time, these studies could not provide much insight into the formation of a deflagration front inside the condensed media. The reaction rates accessible in such RMD simulations were recently embedded into a zero-dimensional continuum scale formulation for studying ignition to deflagration transition in the condensed phase RDX [43].

Due to the timescale and the length scale limitations, a handful of attempts has been made to capture the propagation of a reaction front in the RMD calculations. Wood et al. studied a propagating deflagration wave due to a void collapse in RDX for a very short duration of 60 ps [4]. Sergeev and Yanilkin used a thermal pulse to initiate a combustion wave in PETN [44]. The authors found that the velocity of the combustion front depends upon the crystal orientation and varies linearly with pressure. However, none of these existing RMD simulations provide the details of thermochemistry (mass, energy and species transport) behind the formation and propagation of a reactive deflagration front in the condensed phase energetic materials. The purpose of this work is to demonstrate that RMD can provide the rate of propagation of a deflagration front and the chemistry behind the deflagration using a predictive framework. Traditional continuum scale methods use the Eulerian control volumes (CV) to calculate mass, energy, and species flux across a propagating deflagration front. Averages from RMD simulation can be mapped onto a CV for comparison. A new methodology is developed and demonstrated to enable a comparison between the atomistic deflagration and continuum deflagration models. The RMD simulations are computationally expensive. Thus, the simulations are limited to 1D propagation of deflagration in a nanoscale sample. By setting up comparable probes for the chemistry and the trajectory analysis such as the CV approach, the unique advantage of RMD simulations will be extended to the possible grain level reactive mesoscale simulations in future.

2. Simulation details

2.1. Reactive molecular dynamics

The RMD simulations were performed on the high-pressure γ -phase of RDX with the experimental density of 2.26 gm/cm³. The choice of the γ -phase is based on recent observations which indicated that the chemical decomposition is mostly initiated in the γ -phase over the α -phase under moderate shock compression [45,46]. The starting geometry of the unit cell of the γ -phase was obtained from the density functional theory (DFT) calculations, as implemented in the CASTEP program, and van der Waals corrected DFT-D calculations at the PBE level [47]. The unit cell obtained from the DFT-D calculation was then energy minimized using ReaxFF to relax the atomic positions. The 3x3 unit cells of RDX (3.768 nm × 2.844 nm, 72 molecules) were replicated 20, 40, and 100-times in the z-direction to obtain the supercells. The supercells were 21.86 nm, 43.72 nm and 109.30 nm long with 1440, 2880 and 7200 RDX molecules, respectively (Fig. 1). Traditionally, in energetic materials, the hot spots are defined by their size and the temperature. To mimic a hot spot, 144 RDX molecules in one end of the simulation domain were subjected to a temperature pulse of 2000 K for 15 ps duration using an NVT ensemble. Thus, the size of the hot spot corresponds to 10%, 5%, and 2% of the three su-

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