

INITIAL CHEMICAL EVENTS IN THE ENERGETIC MATERIAL RDX UNDER SHOCK LOADING: ROLE OF DEFECTS

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Abstract. We use the recently developed reactive force field ReaxFF with molecular dynamics (MD) to study the role of voids on the initial chemical events in the high-energy material RDX under shock loading. We find that for strong shocks (particles velocity of 3 km/s) very small gaps (2 nm) lead to important over-heating (~ 1000 K). This over-heating facilitates chemical reactions and leads to a larger production of small molecules (such as NO_2 , NO , OH) than in perfect crystals shocked with the same strength. The chemical reactions occur after the void has collapsed and the ejected material re-compressed rather than when hot molecules are ejected out of the downstream surface.

INTRODUCTION

Understanding the initial chemical events in condensed-phase high-energy materials under shock or thermal loading is among the central problems in detonation theory. The coupling between loading, induced mechanical response and complex chemistry makes the study of such process very challenging and there has been little progress in establishing a molecular level understanding. Such detailed understanding requires following the dynamics of reactions at a resolution in time and space that can only be provided by atomistic Molecular Dynamics (MD). Recently, Manaa *et al.* used MD with atomic interactions obtained using Quantum Mechanics (QM) to study the decomposition of HMX at temperature and pressure close to the CJ point [1]. They found that chemistry occurs very rapidly: the time-scales for H_2O production is ~ 2 ps. Unfortunately QM methods are computationally very intensive, making them impractical to study shock waves (requiring simulations with at least thousands of atoms). Such simulations for energetic materials are now enabled by the recently developed reactive force field ReaxFF [2], that accurately describes complex reactive processes while providing

the necessary computational efficiency to allow the simulation of sufficiently large systems for sufficiently long times. We have recently used ReaxFF to study shock waves on RDX perfect crystals and the initial chemical events induced by them [3]. We found that for sufficiently strong shocks (particle velocity $v_{part} > 3\text{km/s}$) RDX decomposes and reacts to form a variety of small molecules. The time-scales of the initial chemical processes are, again, very fast (picoseconds).

Most solid energetic materials are inhomogeneous and defective (polycrystalline, plastic bonded, with voids) rather than perfect single crystals. The presence of such defects is believed to facilitate detonation initiation under shock loading with defects helping localize the energy in the shock. In this paper we study the propagation of shock waves on defective RDX crystals and the influence of such defects in the initial chemical events using ReaxFF with MD.

ReaxFF REACTIVE FORCE FIELD

Traditional Force Fields describe energetics, structures and vibrations of molecular systems but are unable to describe chemical reactions limiting their

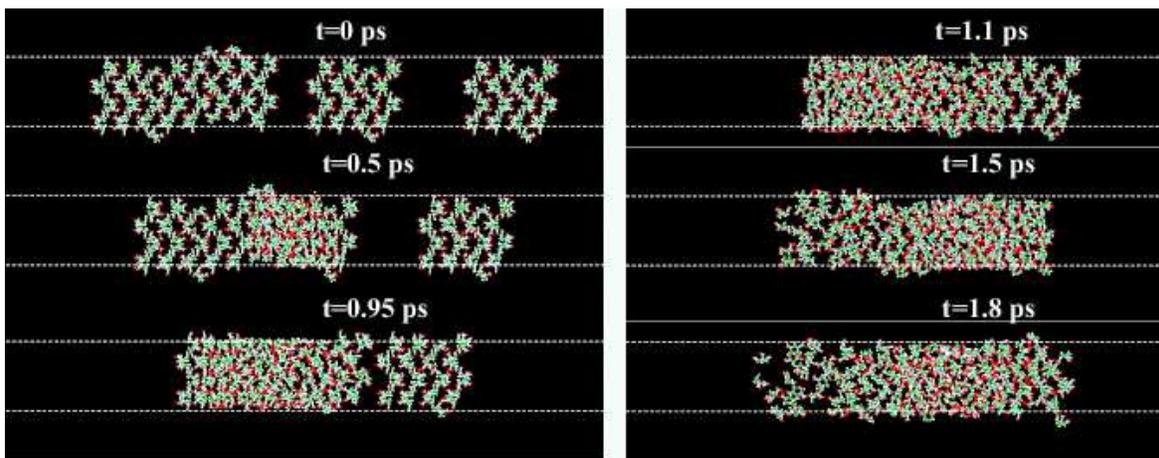


FIGURE 1. Snapshots from ReaxFF MD shock simulation at different times for $v_{part}=3$ km/s and gap width 20 \AA .

range of applicability. This problem was solved to a large extent in recent years with the development of *reactive* Force Fields based on the concept of partial bond order [4, 5, 2]. Furthermore, MD simulations using bond order potentials with simple chemistry can provide valuable information about detonation [5, 6].

The First Principles-based reactive Force Field ReaxFF describes the total energy of an atomic system with three terms [2]:

- **Electrostatic interactions** that allows charge transfer between atoms in response to the atomic environment; charges are calculated self-consistently at every step during MD.
- **Covalent interactions** (bonds, angles, and torsions) based on the concept of partial bond order and calculated purely from atomic positions.
- Shielded **van der Waals interactions** calculated between all pairs of atoms.

It is important to stress that all three type of are defined between every pair of atoms requiring no *a priori* definition of molecule or connectivities. Each atom is described with a unique set of potential functions regardless of its environment.

In order to study RDX the original hydrocarbon ReaxFF [2] was extended to include Oxygen and Nitrogen. ReaxFF has been parameterized against a large number of QM calculations [2, 3] including bond breaking curves for each possible bond, angle

and torsion bending for each possible case as well as several chemical reactions including RDX decomposition mechanisms in the gas phase. ReaxFF accurately describes the gas-phase chemistry of RDX (energies and structures of intermediates as well as transition states) as well as structural and mechanical properties (lattice parameters, bulk modulus and sound speed) [3].

MD SHOCK SIMULATIONS

In this paper we study the role of defects in shock propagation in RDX using high velocity impact MD simulations. We simulate the impact between two two-dimensionally periodic slabs, one of which contains a gap [see Figure 1 (a)] of length l_{gap} . We impose free boundary conditions in the direction of the shock and periodic boundary conditions in the other two directions. The gap simulates the center of an ellipsoid void with two long axes perpendicular to the shock direction [7, 8]. After thermalization, we assigned the desired relative velocity (v_{imp}) to each slab on top of thermal velocities and followed the dynamics with constant energy MD. This arrangement leads to a particle velocity $v_{part} = 0.5v_{imp}$. Figure 1 shows snapshots of the process at different times for $v_{part} = 3\text{km/s}$ and $l_{gap} = 20\text{\AA}$: we can see the initial shock propagation in perfect crystals ($t=0.5$ ps), the molecules ejected from the upstream surface of the gap expanding into the void ($t = 0.95$ ps), and the

ejected material colliding against the remainder of the slab and re-compressing ($t \geq 1.5$ ps). In this paper we will focus on $v_{part} = 3\text{ km/s}$ since for perfect crystals it separates two different regimes: for shocks with $v_{part} > 3\text{ km/s}$ a variety of small molecules are formed while for lower velocities only small fractions on NO_2 are observed [3].

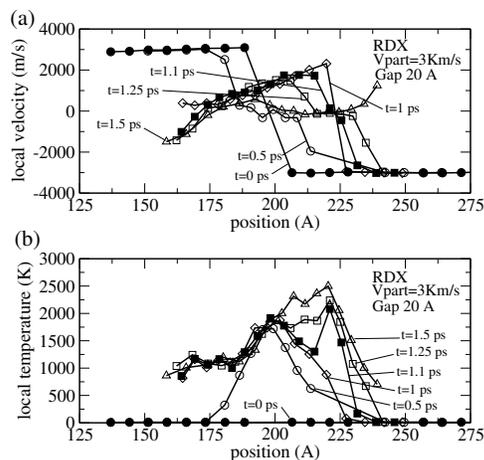


FIGURE 2. Particle velocity (a) and local temperature (b) profiles at different times. Particle velocity 3 km/s, gap width 20 Å.

Figure 2 shows profiles (along the shock direction) of the local particle velocity (top) and local temperature (bottom). In order to obtain such profiles we divide our system into 16 regions, each containing 8 RDX molecules. At $t=0$ ps (filled circles) we see the imposed relative velocities and initial temperature (10 K). At $t=0.5$ ps (open circles) the slabs have collided and two symmetric shock waves are propagating: the velocity of the shocked material is zero and its temperature is between 1500 and 2000 K. From $t=0.75$ ps to $t=1$ ps (open diamonds) the shock on the right slab has already reached the gap and molecules near the upstream surface are accelerated into the void with local velocities relative to the down-stream, un-shocked, portion of the right slab reaching $2v_{part}$. The ejecta from the free surface hits the remainder of the slab at time $1 < t < 1.1$ ps (see filled squares) leading to high local temperatures (see temperature profiles for $t=1.1, 1.25$ and 1.5 ps). We can see from Figure 2 (b) that the local temperature caused by the shock is much higher in the regions surrounding the gap than that in the perfect slab.

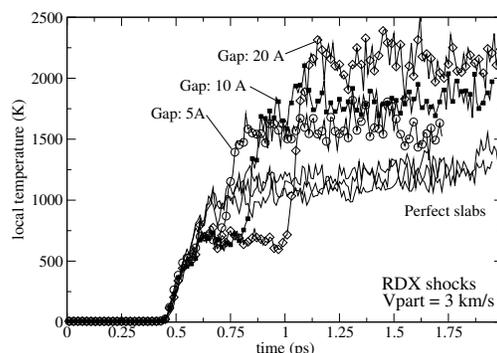


FIGURE 3. Time evolution of local temperature of the last region (8 molecules) the shock goes through in the downstream half of the right slab for $l_{gap}=5$ Å (circles), $l_{gap}=10$ Å (squares), and $l_{gap}=20$ Å (diamonds). We also show that time evolution of the local temperature of the corresponding (mirror) region in the perfect slab (black lines)

In order to study the local heating caused by the interaction of the shock wave and the gap as well as its dependence on gap width we plot in Figure 3 the time evolution of the local temperature of the last region (8 molecules) the shock goes through in the downstream half of the right slab for $l_{gap}=5$ Å (circles), $l_{gap}=10$ Å (squares), and $l_{gap}=20$ Å (diamonds). We also show that time evolution of the local temperature of the corresponding (mirror) region in the perfect (left) slab; the temperatures of the regions in the perfect slab are independent of the gap width and are displayed as black lines. We can see that the initial heating of the regions by the gap is similar to that of the ones in the perfect slab but they reach a lower temperature (independent of gap width) because some of the shock energy is used to accelerate them into the void. When the ejected (expanding) molecules collapse with the upstream part of the right slab (at a time that depends on void width) they re-compress and heat up to temperatures much higher than that attained in the perfect slab. Holian and collaborators proposed a model to explain this overheating based on the re-compression of the evaporated ejecta and validated it with large-scale two dimensional MD simulations Lennard-Jones solids [7]. In agreement with their model we find that heating increases with gap width.

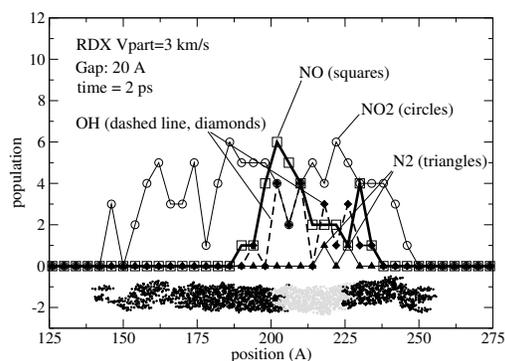


FIGURE 4. Profile of the population of several species for $t=2$ ps. RDX shock $v_{part} = 3\text{ km/s}$, gap width 20 \AA .

Once we have seen local heating due to void-shock interaction the main question is then: is the overheating achieved with these void widths enough to significantly facilitate the chemistry? Figure 4 shows the profiles (along the shock propagation direction) of the population of four small molecules [NO_2 (circles), NO (squares), OH (dashed lines with diamonds) and N_2 (triangles)] at time $t=2$ ps. Black and gray circles below the profiles show the atomic positions at $t=2$ ps differentiating the atoms belonging to the left slab and to both portions of the defective slab. It is clear from figure 4 that the population profiles are very asymmetric with a larger quantity of products formed in the defective crystal. The quantities of NO and OH produced on the defective half are comparable to those obtained in perfect crystals at a higher impact velocity: $v_{part} = 4\text{ km/s}$ [3]. Much larger simulations will be necessary to establish if the enhancement of the initial chemistry observed here is enough to generate a self-sustained detonation and consequently increase the sensitivity of the material or if instead it will die out.

CONCLUSIONS

First Principles-based atomistic modeling of shock loading of high-energy nitramines have become feasible due to the development of the reactive force field ReaxFF. ReaxFF with MD allows full-physics, full-chemistry simulations of shock waves propagating in perfect and defective HE crystals and the

chemical reactions they induced. It is important to stress that no approximation is made as to what type of chemical reactions are allowed or what type of molecules can be formed.

We found that even small gaps (few nanometers) can lead to a local increase in temperature of over 1000 K on top of the shock heating. We have shown that this heating enhances and facilitates the initial chemical reactions. Thus, even small defects can play a key role in reducing the detonation threshold. Future work we will focus on quantifying the decrease in detonation threshold as a function of void size.

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