Shock-induced hotspot formation and chemical reaction initiation in PETN containing a spherical void

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Abstract. We present results of reactive molecular dynamics simulations of hotspot formation and chemical reaction initiation in shock-induced compression of pentaerythritol tetranitrate (PETN) with the ReaxFF reactive force field. A supported shockwave is driven through a PETN crystal containing a 20 nm spherical void at a sub-threshold impact velocity of 2 km/s. Formation of a hotspot due to shock-induced void collapse is observed. During void collapse, NO$_2$ is the dominant species ejected from the upstream void surface. Once the ejecta collide with the downstream void surface and the hotspot develops, formation of final products such as N$_2$ and H$_2$O is observed. The simulation provides a detailed picture of how void collapse and hotspot formation leads to initiation at sub-threshold impact velocities.

1. Introduction

It has been reported that material defects and heterogeneities such as dislocation, porosity, and grain boundaries play key roles in the shock-induced initiation of detonation in energetic materials [1–7]. Several simulation studies have been reported pertaining to nanoscale defect-enhanced chemical reactivity. Nomura et al. reported formation of a hotspot and enhanced chemical reactions in RDX crystal containing a 20 nm spherical void at a sub-threshold impact velocity of 2 km/s. Formation of a hotspot due to shock-induced void collapse is observed. During void collapse, NO$_2$ is the dominant species ejected from the upstream void surface. Once the ejecta collide with the downstream void surface and the hotspot develops, formation of final products such as N$_2$ and H$_2$O is observed. The simulation provides a detailed picture of how void collapse and hotspot formation leads to initiation at sub-threshold impact velocities.

Several works on reactive molecular dynamics (MD) simulations of perfect single crystal PETN have been reported. Budzien et al. [11] investigated chemical reaction initiation in perfect PETN shocked along [100] crystallographic orientation, and a reaction initiation threshold impact velocity of 3 km/s was observed. Zybin et al. [12] studied chemical initiation of perfect PETN under combined shear and compressive load, and they confirmed the model of steric hindrance to shear proposed by Dick et al. [13, 14]. Zybin et al. also reported an initiation threshold impact velocity of 3 km/s along [110] orientation.

In this work, we perform a large-scale reactive MD simulation of a realistic model of pentaerythritol tetranitrate (PETN) single crystal containing a 20 nm diameter spherical void. We drive a supported shockwave through the crystal, inducing void collapse and hotspot formation, and we examine shock-induced chemical reaction initiation.
2. Computational Details

To model shock-induced chemical reactions in our large-scale MD simulations, we use the ReaxFF reactive force field as implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package [15, 16]. ReaxFF is an advanced bond-order based, variable charge force field that enables large-scale simulations of chemically reactive systems. Full details of ReaxFF can be found elsewhere [17–19]. The particular ReaxFF parameterization used in this work was developed for nitramines [20] and was extended to triacetone triperoxide (TATP) [21] and nitromethane [22]. It has been previously applied in several shock simulation studies of PETN [11, 12, 23]. We have shown that this force field description accurately reproduces dissociation barriers of a gas phase PETN molecule along several different reaction channels, reasonably predicts shock properties of PETN crystals including $U_S-U_H$ Hugoniot states and shock initiation stress along different orientations, and explains the dependence of PETN sensitivity on crystal orientation [23].

In this work, we prepare a PETN crystal with a spherical void (containing only vacuum) that is 20 nm in diameter. The system is fully three-dimensional and contains about 8.9 million atoms. The [110] orientation of the PETN crystal is aligned with the $x$-direction of the simulation box. Periodic boundary conditions are applied to the transverse $y$ and $z$ directions, while the $x$-direction is non-periodic. The right end of the crystal in the $x$ direction is treated as a free surface. A reflective wall boundary condition is applied to the left end, which mimics impact with an infinite-impedance flyer plate. The overall sample dimensions of 60.4 nm $\times$ 40.3 nm $\times$ 41.9 nm in the $x$, $y$, and $z$ directions, respectively. A snapshot of the PETN crystal before shock compression is illustrated in figure 1a. After equilibration at 300 K, all the atoms in the PETN crystal are assigned an additional particle/impact velocity ($U_P$) in the negative $x$ direction, colliding it against the reflective wall. In previous work with perfect PETN crystals, it was reported that a minimum impact velocity of 3 km/s was required to initiate chemical reaction [11, 12]. In this study we use a sub-threshold impact velocity of 2 km/s, demonstrating the presence of a void lowers the initiation threshold. Temperature is calculated as a function of position and time by grouping atoms into small cubic regions based on their positions at a

![Figure 1](image-url)

**Figure 1.** Oblique views of the PETN crystal containing a 20 nm spherical void at (a) its initial state and (b) 7.7 ps after impact. Atoms in subfigure (a) color coded by atom type: black is C, white is H, red is O and blue is N. Atoms in subfigure (b) color coded by [110] velocity (axial velocity): navy is $-2$ km/s, cyan is 0 km/s, red is $+2$ km/s. Half of the system was made invisible to show the initial void and the formation of the hotspot due to void collapse.
particular timestep. The temperature of each region is then calculated by summing the kinetic energy of each atom after subtracting the center-of-mass velocity of all the atoms in the region.

3. Results and Discussions
As the crystal collides against the reflective wall, a supported shockwave is driven through the crystal from left to right along the x direction ([110] crystal orientation) causing sudden uniaxial compression of the crystal. A snapshot of the crystal at 7.7 ps after collision is illustrated in figure 1b. Dark blue and light blue regions correspond to uncompressed and compressed PETN crystals, respectively. The boundary between dark and light blue regions indicates the position of the shockwave.

![Figure 2](image)

Figure 2. Sequence of snapshots illustrating the propagation of the shockwave through the PETN crystal containing a 20 nm spherical void. Atoms color coded by [110] velocity (axial velocity): navy is $-2$ km/s, cyan is 0 km/s, red is $+2$ km/s. Half of the system was made invisible to show the shockwave-void interaction.

Illustrated in figure 2 is a sequence of snapshots depicting the propagation of the shockwave through the PETN crystal. The shockwave reaches the upstream void surface after 1.7 ps and the downstream void surface after 7.7 ps. The shockwave reaches the right-end free surface after 10.9 ps, at which point the crystal has been compressed from 60.4 nm to 40.9 nm, or 68% of its initial volume. The average temperature rises from 300 K to 700 K over the course of the simulation. In corresponding plots of 3D temperature variation (not shown) a persistent region with much higher temperature is observed and this region coincides with the original location of the downstream void surface. This high-energy, high-temperature region, or hotspot, is a direct result of shock compression-induced void collapse, jetting of fragments from the upstream void surface, and subsequent collision of the jet with the downstream void surface (see figure 2c). It is estimated that the hotspot is $3340 \text{ nm}^3$ in size, with an average temperature of 1830 K, significantly higher than the temperature of the bulk crystal (near the transverse periodic boundaries), which is 640 K. Localization of thermal energy inside and near the hotspot has a direct impact on chemical reaction initiation.

Plotted in figure 3 is the evolution of major molecular species found in the system. During the first 1.7 ps, the PETN molecules remain largely unreacted. As the shockwave reaches the upstream void surface at 1.7 ps, the PETN concentration starts to decrease, accompanied by the appearance of NO$_2$ molecules. This indicates that NO$_2$ fragments are violently ejected from the upstream void surface by the shockwave. After 5.7 ps these high-velocity molecular fragments collide with the downstream void surface and the chemical evolution of the system undergoes a second inflection point: PETN is consumed much more quickly, numbers of NO$_2$ and NO$_3$ molecules increase more rapidly, and the formation of H$_2$O and N$_2$ molecules begins. This is attributed to the conversion of collision kinetic energy to thermal energy of molecules at the downstream void surface.

Illustrated in figure 4 is a sequence of snapshots depicting the formation of H$_2$O and N$_2$ molecules in the shock-compressed crystal ranging from 5.7 ps when the ejecta fragments first impact the downstream void surface to 10.9 ps when the shockwave reaches the PETN free...
Figure 3. Evolution of major molecular species in a PETN crystal containing a 20 nm void shocked along [110] orientation at an impact velocity of 2 km/s. PETN plotted in the inset. 0 ps on the x-axis indicates time of initial collision with the wall. Upstream void ejecta mainly composed of NO$_2$ (green curve) and NO$_3$ (blue), and these ejecta collide with the downstream void surface at 5.7 ps after impact. Formation of H$_2$O (magenta) and N$_2$ (cyan) occurs only after the upstream/downstream collision.

surface. H$_2$O and N$_2$ molecules are mostly found inside the developed hotspot with only a very few H$_2$O molecules found near the reflective wall boundary, indicating that chemical reactivity is greatly enhanced by the presence of the void. This is consistent with the previously published observation that a minimum impact velocity of 3 km/s is required to initiate reaction in a perfect crystal [11, 12].

4. Conclusions
We performed a large-scale reactive molecular dynamics simulation of shock compression of a 8.9 million atom PETN crystal containing a 20 nm spherical void. We used the ReaxFF force field [17–19] as implemented in the LAMMPS software [15, 16], using an established force field description for PETN [11, 12, 23]. We drove a supported shockwave through the void-containing PETN crystal along its [110] crystal orientation at a sub-threshold impact velocity of 2 km/s. Shock-induced void collapse and subsequent hotspot formation were observed. The average temperature of the hotspot region is approximately 3 times higher than the temperature of the shock-compressed bulk crystal. Ejecta from the upstream void surface were mainly composed of NO$_2$, while the formation of H$_2$O and N$_2$ are mostly found inside the developed hotspot. This indicates that chemical reactivity of the PETN crystal is greatly enhanced by the presence of the void, which causes shock-induced void collapse, ejection of high-velocity fragments from the upstream void surface, and conversion of collision kinetic energy to thermal energy in PETN molecules at the downstream void surface.
Figure 4. H$_2$O (small white spheres) and N$_2$ (large red spheres) molecules in a PETN crystal containing a 20 nm void shocked along [110] orientation at an impact velocity of 2 km/s at (a) 5.7, (b) 7.7, (c) 9.7 and (d) 10.9 ps after impact. [110] orientation is along the red axis, [110] along the green axis, and [001] along the blue axis. Only H$_2$O and N$_2$ molecules are shown; unreacted PETN and all other reaction products are invisible.

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