

DIRECT QUANTUM MECHANICAL SIMULATIONS OF SHOCKED ENERGETIC MATERIALS

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ABSTRACT

Quantum mechanical calculations based on density functional theory (DFT) are used to study dynamic behavior of shocked energetic materials (EM). In this work, we present results of quantum molecular dynamics (QMD) simulations of shocked pentaerythritol tetranitrate (PETN), a conventional high explosive, and the polymeric cubic gauche phase of nitrogen (cg-N), proposed as an environmentally acceptable energetic alternative to conventional explosive formulations. These simulations, made possible through a Challenge grant awarded by the DoD High Performance Computing Modernization Program (DoD HPCMP), represent the leading edge of DFT simulations in both system size and simulation time with over 4000 atoms and up to ten thousand time steps utilizing as many as 512 processors per run.

1. INTRODUCTION

The changing nature of international conflicts requires the transformation of war-fighting capabilities within the Department of Defense. The attainment of the transformation of the military force structure depends on the development of lighter-weight, more robust and integrated armor materials and for systems to meet the requirements for speed, mobility and rapid deployment of weapon platforms and to enhance combat personnel effectiveness and survivability in the face of a widening range of more lethal and countering threats. New energetic materials, with substantially enhanced performance and reduced vulnerabilities, must be developed for future weapons systems to meet these criteria. Advanced Energetic Materials (AEM) are required to enable high priority military missions ranging from Hard and Deeply Buried Target Defeat, to Advanced Propulsion, to lightened highly mobile force evolution and the thrust towards miniaturized munitions and systems. It is recognized that weapons superiority is dependent on the development of AEM since they are key to enhanced lethality and survivability in logistical and tactical environments. Current developmental strategies for formulation of advanced EMs focus on either (1) tailoring the dynamic response of existing EMs that would permit optimal performance with minimal vulnerability for a wide range of future gun, missile, warhead, active protection systems and emerging weapons concepts; or (2) increasing energy content in

candidate materials by introducing or increasing molecular strain within the molecules. With regard to the first strategy, it is imperative that the fundamental mechanisms controlling conversion of the material to product be completely understood; such information could then be exploited to tailor the material or weapon to control the dynamic response. In addressing the second strategy, in which energy content is increased by introducing strain, conventional strategies currently applied to existing EMs must be discarded in favor of completely new types of materials due to limitations on the amount of strain that can be imposed without destabilizing the system [Dlott, 2004]. One potential new class of EM involves high pressure phases of covalent solids, in which structural energy is trapped in metastable states. If the stored structural potential energy can be liberated quickly enough, it is possible that explosion can occur with energies several orders of magnitude larger than conventional explosives. Subsequently, these materials could provide enhanced or configurable performance in advanced weapons applications.

To explore these emerging candidate materials and to obtain a fundamental understanding of the response of an EM to shock, we have performed quantum mechanical calculations based on density functional theory (DFT) to study dynamic behavior of both conventional and novel shocked energetic materials (EM). In this work, we present results of quantum molecular dynamics (QMD) simulations of shocked pentaerythritol tetranitrate (PETN), a conventional high explosive, and shocked polymeric nitrogen (cubic gauche, cg-N) proposed as an environmental acceptable energetic alternative to conventional EMs. While nitrogen seems far-removed from conventional EMs (which are typically large, polyatomic organic molecular crystals, as seen in our depiction of the simulation cell used for PETN in Fig. 1),

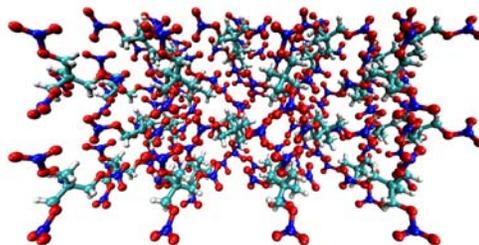


Figure 1. Snapshot of the equilibrated PETN system used in the QMD simulations.

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under pressure it has been shown to take on a polymeric form. The cg-N form is a bulk three dimensional covalent network like diamond, in which every atom has three neighbors compared to diatomic molecular forms of nitrogen (Fig. 2).

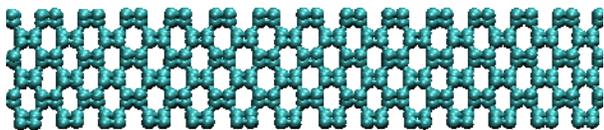


Figure 2. Snapshot of the equilibrated cg-N system used in the QMD simulations.

Since diatomic nitrogen has the strongest bond in nature, the amount of energy released from the polymeric form as it transitions to the more stable standard state is extremely large. The products of the conversion are very simple; the solid, which is composed of singly-bonded nitrogen, transitions to the diatomic triply-bonded gaseous form and small chains. The amount of energy available for release through complete conversion is several times that of the conventional explosive cyclotrimethylene-trinitramine (RDX) by weight and volume. Simulation has confirmed that cg-N is stable at low temperatures and pressures, but will react very rapidly and release large quantities of energy when sufficiently perturbed [Mattson, 2003]. The simplicity and reactivity of this single-element system make it an ideal physically realistic test case for simulation of shock initiation in a material trapped in a high-pressure metastable state. In addition to presenting results for shocked conventional and notional EMs, this paper will briefly describe the theoretical methods, the computational details, software explored to enable adequate treatment of the calculations, and results of the calculations to date.

2. COMPUTATIONAL DETAILS

DFT is not considered the most accurate QM method available, but it has become a state-of-practice in the scientific community due to its computational efficiency relative to other, more accurate methods. For example, the CCSD(T) [Kimmel, 2002] quantum chemistry techniques are formally $O(N^7)$ where N reflects the number of electrons in the system in sharp contrast to DFT methods which typically range from $O(N)$ – $O(N^3)$. In the DFT formalism each electron is treated independently and interacts with other electrons not directly but only through an effective potential which is a function of the total charge density. This mean-field approximation drastically reduces the computational effort compared to higher level quantum chemistry methods while maintaining accuracy sufficient for many applications. Advances in approximations, efficient mathematical algorithms, and implementations on

scalable platforms have further increased application of DFT to large and complex systems of interest to the DoD. In this study, we have utilized the PBE [Perdew et al., 1996] form of the Generalized Gradient Approximation (GGA) of the DFT as implemented in the local orbital basis code CP2K. For nitrogen we have used the double-zeta valence polarization basis (DZVP) which corresponds to a total of thirteen basis functions per nitrogen atom. Total energies and forces were converged to 1.6×10^{-4} and 2.6×10^{-5} a.u., respectively, and were used throughout these calculations.

Two sets of simulations were performed. The first is a DFT molecular dynamics (MD) simulation of a filament of material subjected to flyer-plate impact. This is a non-equilibrium molecular dynamics (NEMD) simulation in which the dynamic response of the material can be directly observed through monitoring the time progression of atomic positions and velocities. These simulations were used to study PETN and cg-N. The second set also utilizes DFT-MD, except the simulations calculate properties of the material under thermodynamic equilibrium at various conditions. Equation-of-State (EOS) information is obtained from these simulations and used to generate the shock Hugoniot, a special set of points satisfying the conservation equations of mass, momentum and energy across the shock front between the quiescent crystal and its final shocked state. This information will be generated using the Erpenbeck [Erpenbeck, 1992] approach, named after an author who used classical MD to generate the shock Hugoniot of a simple model material. The shock Hugoniot was calculated only for cg-N, due to inherent deficiencies in DFT to adequately describe conventional molecular organic crystals (such as PETN) at low compression [Byrd et al, 2004]. These limitations in DFT do not affect the cg-N, a covalently bound system.

2.1. Direct Shock Simulations

In both PETN and cg-N simulations, the simulation cells are composed of the material in an equilibrated configuration. The simulation cell for cg-N consists of a filament of energetic material composed of 2304 atoms arranged in the equilibrium cg-N configuration at $T=250$ K, $P = 1$ atm. The initial simulation cell for PETN is composed of an $8 \times 2 \times 2$ block of unit cells, with the molecules arranged in the experimental configuration and atomic velocities assigned to correspond to room temperature. Because DFT does not adequately describe PETN at the ambient state, we equilibrated the simulation cell at a fixed volume corresponding to the experimental values at room conditions. Atomic velocities were initially assigned to the atoms to correspond to room temperature. All other degrees of freedom were allowed to relax. For the shock simulations, periodic boundary conditions are imposed in the two directions

perpendicular to the direction of shock propagation. In this study, the shock wave will initiate at the far left edge of the filament (see Figs. 1 and 2) and propagate from left to right. Initial velocities consistent with the desired flyer plate impact velocity are assigned to the atoms within a small segment of the material at the far left edge of the filament. The remaining atoms in the filament are at a thermodynamic equilibrium, with the exception of a small rigid block of atoms at the far-right-edge of the simulation cell. This is to ensure that the surface effects at the free edge will not influence the shock propagation. The resulting integration of the microcanonical equations of motion using DFT-MD for this set of initial conditions will simulate shock initiation through flyer-plate impact. The position of the shock discontinuity through the filament is monitored, and when it approaches the end of the filament (i.e. the atoms that are fixed), additional material will be inserted before the fixed atom region, ahead of the progressing shock wave. The state of the material that is added is also in thermodynamic equilibrium and its atomic arrangements are consistent with that of unshocked material at that thermodynamic state.

Since a shock wave travels faster than the sound speed of the material, there is no need to simulate large portions of undisturbed material ahead of the shock front; rather, we have found in earlier classical MD studies that adding material ahead of the propagating shock front is sufficient to adequately describe the dynamics of the process. This method has been used in many classical MD simulations of shock waves [Rice, 1998]. Obviously, in such a simulation scheme, the simulation size grows as the shock wave progresses through the material, significantly increasing the computational demands during the simulation.

2.2 Evaluation of the Shock Hugoniot

The thermodynamic quantities of a material in the quiescent and final shocked states are related by the conservation equations of mass, momentum, and energy across the shock front, and are represented by the shock Hugoniot, a set of EOS points that satisfy the Hugoniot function:

$$H_g(T, V) = 0 = E - E_0 - \frac{1}{2}(P + P_0)(V_0 - V) \quad (1)$$

In this equation, E , P , and V are the internal energy/unit mass, pressure, and volume/unit mass, respectively. E_0 , P_0 , and V_0 are the internal energy/unit mass, pressure and volume/unit mass in the quiescent state. The procedure for identifying points on the shock Hugoniot using the method of molecular dynamics is straightforward [Erpenbeck 1992]. For each volume, a series of DFT-MD simulations of the NVT ensemble are performed over a range of temperatures. Once convergence of the

thermodynamic properties is reached for each simulation, the Hugoniot function is evaluated. The resulting set of calculations will produce a series of $H_g(T)_V$, which is then fitted to a polynomial from which the Hugoniot temperature (T_{Hg}) can be identified from $H_g(T_{Hg})_V = 0$. Once this has been done, the dependence of either the pressure or the internal energy on temperature can be determined through fitting these quantities to polynomials and evaluating them at T_{Hg} . Each of the calculations used to construct the shock Hugoniot for cg-N was composed of 256 atoms, with their initial arrangement consistent with that of the cg-N structure at $T=298K$, $P = 1$ atm. Each trajectory was first equilibrated for 4000 time steps and thermodynamic values were averaged over the subsequent 4000 time steps (1 time step= 1 fs).

3. RESULTS

Two types of MD calculations were performed to provide insight into the nature of shocked cg-N. The less computationally demanding is the generation of the shock Hugoniot using equilibrium MD methods. This methodology does not require large numbers of atoms, and uses MD to generate the EOS for the materials. Its computational cost comes from the number of EOS points needed to map out the shock Hugoniot. Each point on the shock Hugoniot was obtained by interpolating the Hugoniot function for four EOS points. In total this has required in excess of 500,000 CPU hours on the SGI Origin 3900 at AFRL MSRC.

As evident in Fig. 3, no anomalous behavior was found in the principal shock Hugoniot for cg-N.

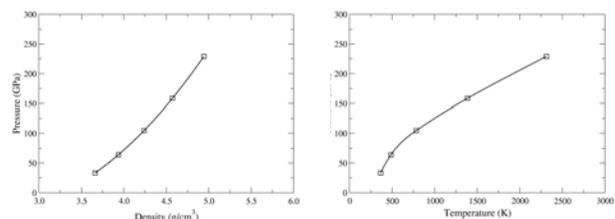


Figure 3. Principal shock Hugoniot of cg-N in pressure-density (left) and pressure-temperature (right) planes.

However, additional NVT simulations showed that cg-N will undergo a phase transition at approximately $P = 50$ GPa, $T = 4000K$; the material transitioned from the polymeric solid form to liquid composed of both atoms and molecules. The material in this state is not well characterized. Figure 4 shows three snapshots of the system at various time steps during the trajectory integration. The left-most frame shows the system in the initial cg-N arrangement, and the right-most frame shows a distribution of atoms and clusters ranging in size from two to ten atoms. The structure of the material is consistent with a liquid.

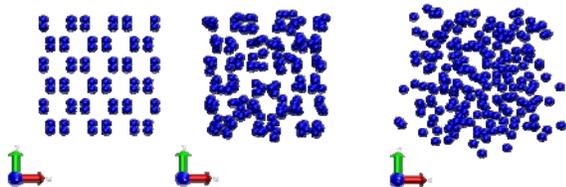


Figure 4. Snapshots of cg-N undergoing a phase transition at $t=0$ (left-most frame), $t=0.35$ ps (middle frame) and $t=0.7$ ps (right-most frame) at $T=4000$ K, $P=50$ GPa.

The dynamic behavior of the material during this portion of the trajectory shows that the clusters are not stable as the atoms rapidly change partners. It is not known whether any true cluster formation is obtained. The middle frame is representative of a transient state of the material that appears to have some structure. Further calculations are needed in order to make a definitive characterization of the transient and final states of the material.

Our first shock simulations were performed on the polymeric form of nitrogen. We have simulated shock wave propagation through the cg-N. The mechanical shocks were initiated by impacting the crystal with a low flyer plate initial velocity to determine the influence of a mild perturbation to this metastable state. Simulations in which periodic boundary conditions are imposed in all dimensions were performed; however, in one type of simulation a vacuum is placed behind the flyer plate. In the other type, no vacuum is present. In both types of simulations a small segment of crystal (54 atoms) on the opposite end of the crystal are held fixed. The results of shock wave simulations using the two types of simulation cells (i.e. with or without a vacuum behind the flyer plate) produced different results. For periodic systems without a vacuum behind the flyer plate or defects, low-velocity impacts were insufficient to produce reaction within the crystal. Rather, the shock wave merely traversed the filament between the flyer plate and the rigid material at the opposite side of the cell several times, with no reactive events. However, reactive events were observed in the simulations in which a vacuum was present behind the flyer plate (Fig. 5).

However, this reaction does not occur upon shock wave compression and subsequent expansion. After reaching the rigid slab of molecule, the shock was reflected back through the shocked material. Upon reaching the left-most edge of the simulation cell, the material at the free edge of the crystal unraveled in chains of up to ten nitrogen atoms. These chains subsequently decompose into azide and diatomic nitrogen molecules, as shown in Fig. 5.

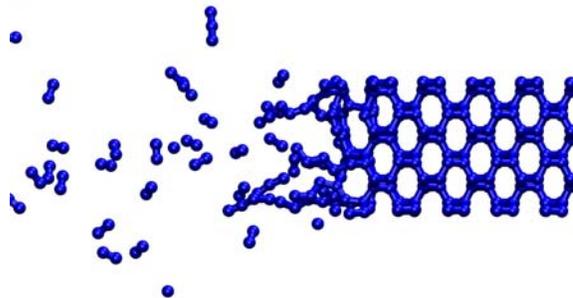


Figure 5. Snapshot of the free edge of the shocked cg-N at $t=3.6$ ps.

QMD simulations of the filament with the free edge under equilibrium conditions (i.e. no shock, 250 K, 1 atm) does not produce unraveling of the free edge, although the filament undergoes an expansion and the atoms at the edge are more mobile. It appears that the unraveling of the material and its subsequent decomposition into tri- and diatomic molecular species is a result of the reflected shock wave. We are continuing further simulations in which the shock wave is not allowed to reflect.

We are repeating the same procedure for the conventional energetic material pentaerythritol tetranitrate (PETN). We have completed the equilibration, and are running the shock wave simulations. The four snapshots in Fig. 6 show the system at the beginning of the trajectory (top-most frame), 0.109 ps (second frame), 0.28 ps (third frame), and 0.418 ps (bottom frame) during the trajectory.

To date, the shock wave has traversed the filament and reached the rigid slab of molecules at the far-right edge. PETN is considerably more complex than cg-N due to the number of degrees of freedom and types of reaction products. The structural nature of PETN, which is a weakly bound molecular crystal in which energy release is due to chemical reaction, differentiates it from cg-N, a covalent solid in which the energy release is due to a phase transition. Therefore it is not surprising to see that the reaction mechanisms described for cg-N are not the same. These differences are apparent in the series of snapshots shown in Fig. 6. In the second frame ($t=0.109$ ps), the shock wave has started to traverse the material, and the material behind the shock front has begun to expand. In the third frame ($t=0.28$ ps), the region through which the shock wave has passed appears compressed and disordered, and reaction products such as NO_2 and OH, as well as some radical fragments of the PETN skeleton, are evident. Finally, at $t=0.418$ ps, we see a material profile that suggests rarefaction in the density; reactions are clearly evident in this region.

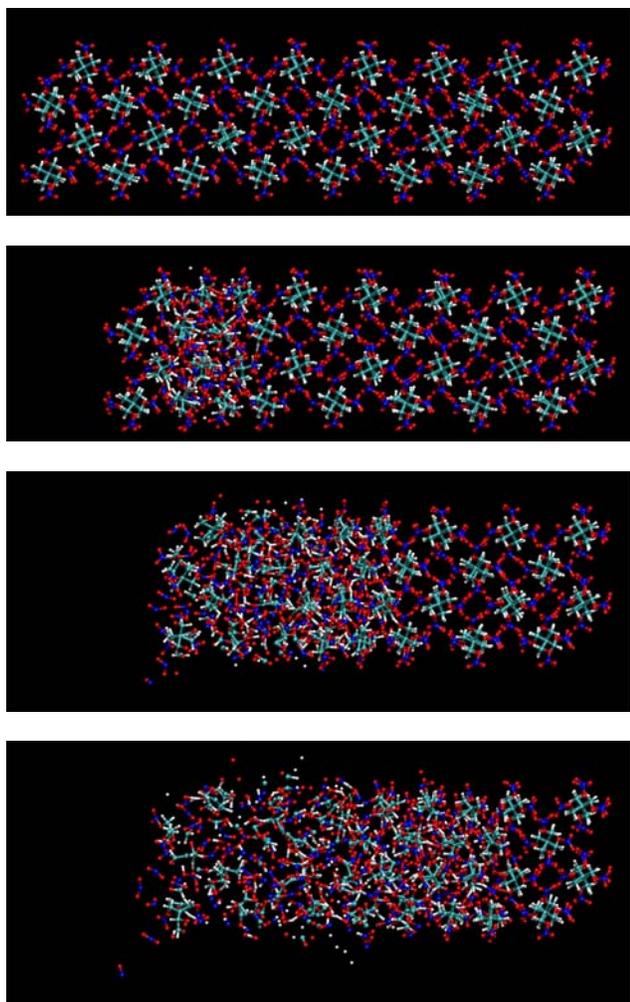


Figure 6. Snapshots of the PETN system at $t=0$ (top-most frame), 0.109 ps (second frame), 0.28 ps (third frame), and 0.418 ps (bottom frame).

To our knowledge, these are the largest DFT simulations of an energetic material that have ever been performed.

CONCLUSIONS

Quantum MD simulations have been used to provide an atomic-level description of the material response of a conventional explosive, PETN and a novel candidate energetic material, a polymeric form of solid nitrogen known as cg-N, to shock. Both simulations showed reactions after passage of the shock wave; however, the mechanistic details differed. PETN reaction occurs through dissociation of NO_2 , OH, and transient reactive molecular radicals, whereas the cg-N material at the free edge of the shocked material unraveled in chains that subsequently decomposed into di- and tri-nitrogen molecules. Additionally, we calculated the shock Hugoniot of cg-N, for future comparison with results from direct shock simulations. These calculations

represent the largest QMD simulations on explosives to date.

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