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## **Enabling R&D for Accurate Simulation of Non-Ideal Explosives**

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# Enabling R&D for Accurate Simulation of Non-Ideal Explosives

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Computational Thermal and Fluid Mechanics

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## Abstract

We implemented two numerical simulation capabilities essential to reliably predicting the effect of non-ideal explosives (NXs). To begin to be able to treat the multiple, competing, multi-step reaction paths and slower kinetics of NXs, Sandia's CTH shock physics code was extended to include the TIGER thermochemical equilibrium solver as an in-line routine. To facilitate efficient exploration of reaction pathways that need to be identified for the CTH simulations, we implemented in Sandia's LAMMPS molecular dynamics code the MSST method, which is a reactive molecular dynamics technique for simulating steady shock wave response. Our preliminary demonstrations of these two capabilities serve several purposes: i) they demonstrate proof-of-principle for our approach; ii) they provide illustration of the applicability of the new functionality; and iii) they begin to characterize the use of the new functionality and identify where improvements will be needed for the ultimate capability to meet national security needs. Next steps are discussed.

## **ACKNOWLEDGMENTS**

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## Nomenclature

ANFO	Ammonium Nitrate Fuel Oil
DOE	Department of Energy
EOS	Equation of State
HE	High Explosive
HME	Homemade Explosives
HVRB	History Variable Reactive Burn model
IED	Improvised Explosive Devices
MD	Molecular Dynamics
MSST	Multiscale Shock Technique
NX	Non-ideal Explosive
R-H	Rankine-Hugoniot
SNL	Sandia National Laboratories

# 1. INTRODUCTION

Homemade explosives (HME) and improvised explosive devices (IEDs) are an increasing domestic threat and are commonly used in foreign conflicts dominated by sectarian disputes and/or non-state terrorists. Protection or counter-measures against these weapons could be significantly improved with a better technical understanding of their behavior. Termed “nonideal” explosives (NX) because their behaviors are not well represented by classical, one-dimensional, steady detonation theory, relatively little fundamental research has been performed to characterize them and predictive numerical modeling is largely absent. An improved level of understanding relies on tightly coupled pursuit of experiment, theory, and numerical modeling. In particular, numerical modeling is essential for the discovery of reaction mechanisms and simulating the coupled, nonlinear evolution of composition, temperature, and pressure of the reactive flow behind a shock front in a highly heterogeneous continuum; particularly at extreme conditions that are not readily accessible by current experiment measurements.

Ideal explosives are commonly modeled using a phenomenological description incorporating a single reaction progress variable that averages the equations of state of unreacted and fully-reacted materials. This “two-state” assumption is adequate for many applications of ideal explosives in which the chemical reactions are sufficiently rapid to support the shock front and form a steady detonation wave. Non-ideal explosives have a much thicker reaction zone that causes a significant deviation from ideal behavior and is a result of multiple chemical reaction paths that have slower kinetics. The shortcomings of the traditional models of detonation in application to NXs are linked to the use of overly simplified chemistry, disregard of their kinetics, and inaccurate descriptions of mixed equations of state that are used for partially-reacted states. Thus, the partitioning of energy that supports a shock front and flow expansion is not accurately represented. Better descriptions are needed to incorporate the multiple reaction paths of the actual chemistry and the effects of these reactions on the rate of energy release.

While the predictive simulation of NXs will require accurate treatments of diverse phenomena across the multiple scales of atomistics, microscale, mesoscale, and the engineering continuum scale, a staged approach should begin by focusing on two tasks: i) Extend the chemistry treatment in conventional hydrocode simulation of reactive flow from two-state to multi-state descriptions for non-ideal energetic materials; ii) Extend classical molecular dynamics capabilities for discovery and characterization of reaction pathways in nonideal explosives. Task (i) is needed to go beyond the two-state model of reaction to more accurately represent that actual chemistry and kinetics and do so with the flexibility for the extent of reaction to vary spatially throughout a simulation. Task (ii) can provide detailed reaction paths through use of recently developed reactive MD methods. These simulations with atomistic resolution can reveal the succession of intermediate chemical species that form, further react, and the rates of these chemical transformations. A subsequent step, once the multiple, detailed reaction paths for a given NX are identified will be to abstract from that information the dominant and rate-limiting reactions, and devise an approximate representation of these reactions in a reduce network of chemical reactions – a chemical constitutive equation – that can be exercised in a continuum shock wave physics simulation with reasonable efficiency. Development of such a reduce reaction network was beyond the scope of the present project.

Even these two near-term tasks are significant research endeavors. Hence, for this brief study, we implemented two numerical simulation capabilities essential for achieving these near-term tasks. We also performed preliminary demonstrations of these two capabilities for several purposes: First, to demonstrate proof-of-principle for our approach; second to provide information useful for illustrating the applicability of the new simulation functionality; and third, to begin to characterize the use of the new functionality and identify where improvements in efficiency or extension of capability will be needed for the ultimate capability to meet national security needs.

## 2. APPROACH AND ACCOMPLISHMENTS

As a step toward establishing a reliable, physics-based simulation capability for non-ideal explosives, we implemented the TIGER [1] thermochemical equilibrium code as an equation of state (EOS) in-line routine in Sandia's CTH shock wave physics code [2]. We also implemented an additional technique for simulating steady shock wave response, called the MSST method, into Sandia's massively parallel molecular dynamics code LAMMPS [3]. Both CTH and LAMMPS are widely used in their respective R&D communities across DOE, DoD, and at multiple universities.

### 2.1. TIGER EOS

The TIGER thermochemical equilibrium code was implemented into CTH as a primary equation of state. This implementation is compatibility with all existing reactive flow models in CTH. We also made improvements to the equilibrium solver within TIGER to start to make it more robust and efficient. We have also implemented new commands to the TIGER code to allow multiple atomic populations to be specified and to allow for implementation into the parallel architecture of CTH.

Implementing TIGER into CTH entailed the following changes and additions to the code:

- A. TIGER was developed in the mid-1970s and is written in FORTRAN IV. CTH is written in FORTRAN 90 and we were able to compile TIGER using a FORTRAN 90 compiler.
- B. TIGER is incorporated into the current version of CTH and goes through the routine testing and benchmarking of the code. This assures us that the addition of TIGER has not disturbed the previously existing operation of CTH and that the new capability remains functional as the code changes.
- C. Within CTH, TIGER now executes in parallel and handles multiple materials.
- D. New commands were added to TIGER to calculate detonation states of explosives and fit to a standard JWL equation of state model. The TIGER output information on chemical species, temperature, and pressure were added to the CTH database for analysis and plotting.
- E. Some of the constructs of FORTRAN IV do not properly compile with newer Fortran 90 compilers. We identified and modified routines as necessary. A lot of effort went in to modifying the equilibrium solver. We reorganized the routine for clarity and unraveled some of the assumptions concerning the species database ordering. By manipulating the species ordering we were able to improve the efficiency of the solver.
- F. Began address robustness and efficiency by implementing a backup capability for TIGER and alternate algorithms for generating trial solutions that initiate the iterative equilibrium solve.

### 2.2. MSST Method for Determining Shock State

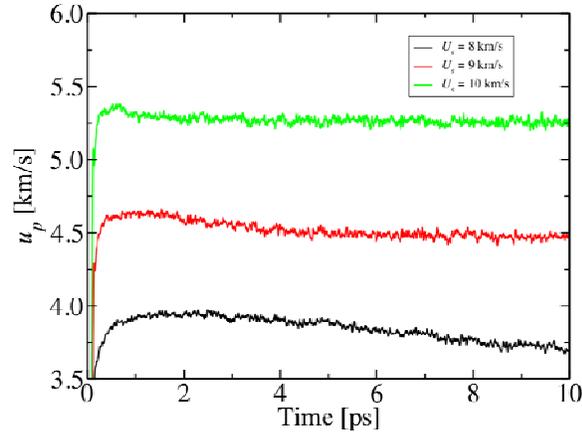
Molecular dynamics simulations with a reactive interatomic potentials can be used to study the initiation of detonation in energetic materials. There are several ways to do this. We used the so-called direct method in a previous study of PETN (pentaerythritol tetranitrate) [4]. A

high-impedance wall was driven into a slab of PETN crystal, causing a shock wave of pressure and chemical reactivity to propagate through the crystal. The ReaxFF reactive interatomic potential was used to represent the behavior of PETN molecules [5]. We simulated two different impact velocities: 3 km/s and 4 km/s, producing shock waves propagating at speeds higher than the steady state detonation speed; *i.e.*, overdriven shock waves. Passage of these shock waves imparted a particle velocity of 3 km/s and 4 km/s, respectively, to the material. We tracked the shock waves for 70 ps (3 km/s impact) and 35 ps (4 km/s impact), using about 500,000 atoms in each case. The total cost of these two simulations was about 100 CPU-years. Because we had to constantly add fresh material in front of the advancing shock wave, the computational cost increased quadratically with the duration of the simulations.

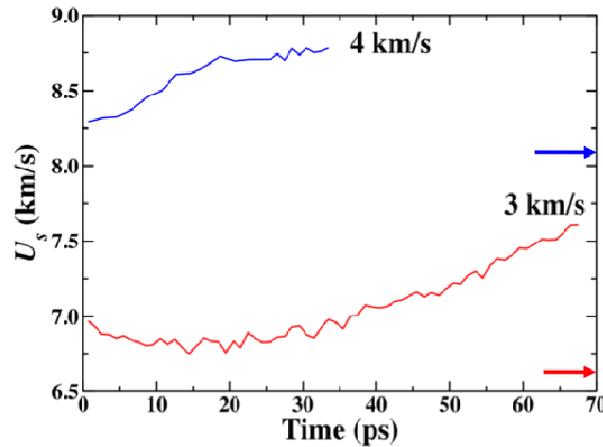
Rather than study the shock wave moving through an ever-growing slab of material, it would be far more efficient to track the time-evolution of a representative cell of material as it moves through the shock wave. This is akin to switching from an Eulerian to a Lagrangian frame. One method for doing this is to use the Hugoniot method [6] in which the peak stress of the shock state is specified, as opposed to specifying the particle velocity of the shock state, which the direct simulation method affords. The Hugoniot method was previously implemented in LAMMPS and offers certain advantages, but is not fully satisfactory. In order to have an alternative to the Hugoniot method, we implemented the Multiscale Shock Technique (MSST) in LAMMPS, in collaboration with Evan Reed of Stanford University, one of the original inventors of the method [7]. The equations of motion of the atom coordinates and the dimensions of the simulation cell are modified to enforce the Rankine-Hugoniot (R-H) equations of mass, energy and momentum conservation, assuming a specified, steady state shock speed, as opposed to the peak stress, as in the Hugoniot method. The momentum R-H condition constrains the cell to undergo uniaxial compression along the Rayleigh line, whose slope is determined by the specified shock speed. The energy R-H condition serves to constrain the temperature of the cell, and the mass R-H condition determines the material velocity of the cell relative to the initial state.

In order to test the underlying assumptions of the MSST method, as well as the validity of the LAMMPS implementation, we ran MSST simulations for PETN with the same ReaxFF potential and initial crystal configuration as used in the previous direct simulations. MSST simulations were run with shock wave speeds of 8, 9, and 10 km/s along the [100] crystal axis. These *shock wave* speeds should produce steady shock states in which the material is moving with *particle* velocities comparable to those prescribed in our direct simulations. The initial cell consisted of a 4x4x4 supercell of PETN crystal with 3712 atoms, equilibrated at 300 K.

We observed that in all three cases, the particle velocity increased rapidly to a peak value, before falling slowly to a somewhat lower final value (Figure 1. Material velocity evolution using MSST. Figure 1). This is consistent with the behavior observed in direct simulations, where the observed shock speed initially decreased before slowly increasing (Figure 2). We have conjectured that this behavior is due to initial energy absorption in endothermic reactions forming intermediate species, followed by net energy release in exothermic reactions forming product species.



**Figure 1.** Material velocity evolution using MSST. Note initial rapid rise followed by slow decline to a constant value.



**Figure 2.** Shock velocity evolution using direct simulation. Arrows are estimates of corresponding MSST shock speeds.

In order to quantitatively compare the shock speeds in direct and MSST simulations, we observe that the peak particle velocity increases linearly with MSST shock speed. Inverting this relationship, we can estimate the MSST shock speeds that would produce peak material velocities of 3 km/s and 4 km/s (see red and blue arrows in Figure 2). These estimates lie very close to the initial shocks speeds observed in the direct simulations.

We can also compare many other quantities between the two simulations, such as stress, temperature, and chemical composition. For these quantities, we have observed qualitative agreement between the MSST results and direct simulations. In order to make a more precise comparison, we plan to extend the MSST calculations out to the 100 ps timescale achieved in the direct simulations. Because the number of particles in MSST is independent of the timescale, this will require only about one one-hundredth the amount of CPU time used for the direct simulations.

### 3. DISCUSSION AND FUTURE WORK

While we have made substantial progress in this brief effort, TIGER executes slowly from within CTH. Substantial improvements in efficiency are needed to make it practical to use TIGER on-the-fly as is needed for a predictive simulation capability for NXs. To achieve predictive simulations of the network of competing, multi-step reaction paths that contribute to the detonation of NXs, the determination of chemical equilibrium states with TIGER will provide good estimates of the spatially varying, time-dependent energy released. The amount of energy released is a key quantity needed to simulate the evolution of the shock and expansion waves and, in particular, their interactions with boundaries.

Applying the desired simulation capability to treat any given NX will additionally require generating a manageably small network of reactions that represent the chemistry of the NX with sufficient accuracy. The newly acquired MSST method and the Hugonostat method that was already in hand, in combination with recently developed reactive interatomic potentials, are expected to enable fairly routine determination of detailed reaction paths for a NX. However, more work is needed to flesh out this approach to determining the multi-step chemical reactions. Next steps include exercising the MSST and Hugonostat methods to longer times to determine detailed set of reactions and validating these against known reaction networks. Then, optimization algorithms will need to be developed for automatically and efficiently reducing this reaction path information into a form that is manageable in the CTH continuum shock physics simulation.

Once we have a reliable reactive material model to represent a pure, fully dense sample of a NX, it can be used in CTH simulations to characterize the additional effects of any mesoscale structure, as fabricated, on the actual behavior of macroscopic specimens of the material. For example, ANFO has a complicated mesoscale structure which is an aggregate of small spherical prills penetrated by fuel oil. In separate work, M. Baer of Sandia Labs has applied methods he pioneered [8] with CTH to resolve the fine-scale, heterogeneous continuum structure of ANFO to begin exploring how the detailed behavior of the aggregate develops into the overall, macroscopic response of this NX. Similar characterization using fine-scale continuum simulations will be needed for other NXs that have pronounced microstructure.

Numerical simulation of microstructural effects cannot be relied on without proper validation. Validation of microstructural effects is a two-fold research challenge. First, there are few controlled experiments that can be performed to quantify microstructural effects. Second, for these experiments there are only a few diagnostics available with which to make observations. Efforts are needed to develop additional experiments and diagnostics that would improve the validation process. Similarly, development of experiments and diagnostics for characterization of properties and discovery of phenomena would greatly aid the beginning steps of computational model development for the reactive dynamic response of NXs. Moreover, because their response results from phenomena occurring on several length and time scales, discovery measurements are needed that are revealing of the phenomena at different, specific scales.

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