Reactive atomistic simulations of shock-induced initiation processes in mixtures of ammonium nitrate and fuel oil

Aidan P. Thompson and Tzu-Ray Shan
Sandia National Laboratories, Albuquerque, NM 87185, USA
E-mail: atomps@sandia.gov

Abstract. Ammonium nitrate mixed with fuel oil (ANFO) is a commonly used blasting agent. In this paper we investigated the shock properties of pure ammonium nitrate (AN) and two different mixtures of ammonium nitrate and n-dodecane by characterizing their Hugoniot states. We simulated shock compression of pure AN and ANFO mixtures using the Multi-scale Shock Technique, and observed differences in chemical reaction. We also performed a large-scale explicit sub-threshold shock of AN crystal with a 10 nm void filled with 4.4 wt% of n-dodecane. We observed the formation of hotspots and enhanced reactivity at the interface region between AN and n-dodecane molecules.

1. Introduction
Ammonium nitrate (NH$_4$NO$_3$, abbreviated as AN hereafter) is a strong oxidizer. When mixed with an oxidizable material such as fuel oil, it forms a low-cost, moderately powerful explosive. In the solid phase AN exists as an ionic crystal composed of monovalent polyatomic NH$_4^+$ and NO$_3^-$ ion pairs, while in the gas phase it exists as neutral acid-base pairs [1]. Five well-characterized AN crystal phases exist at atmospheric pressure. The highest temperature phase I is thermodynamically stable above 170 C, while the lowest temperature phase V is stable below -20 C [2–8]. Phase IV is the stable phase at room temperature and atmospheric pressure. AN becomes an explosive when mixed with a few percent of fuel oil (ANFO, ammonium nitrate fuel oil), which is widely used in mining, excavation, and other industrial activities [9].

Several experimental studies using polycrystalline, granular samples [10–13] have been reported pertaining to the static and dynamic loading of AN. Shock Hugoniot states expressed in the form of a linear relationship between shock velocity $U_S$ and particle velocity $U_P$ have been reported. These experimental principal Hugoniot states for unreacted AN are summarized in table 1. In addition to these experimental efforts, several modeling and simulation studies have been published [1,14,15]. For ANFO, Davis and Hill reported the Jones-Wilkins-Lee equation of state, particularly the expansion isentrope on the P-V plane, of prilled ANFO at a density of 0.93 g/cc using cylinder experiments [16], while Souers et al. investigated the effects of containment on detonation velocity of emulsified ANFO at 1.07-1.16 g/cc densities using a simple reactive flow hydrodynamics model [17].

In this paper we present results for shock compression and shock-induced chemistry of AN/ANFO using large-scale reactive molecular dynamics simulation. We use the ReaxFF
reactive force field [18,19] description for AN/ANFO, and we utilize both the Multi-scale Shock Technique (MSST) [20] and also explicit non-equilibrium molecular dynamics (NEMD). For MSST, shock Hugoniot states and shock-induced initiation pathways of AN and ANFO are presented. Using explicit NEMD, we simulated shock of AN containing a 10 nm void filled with n-dodecane. The ReaxFF MD simulations are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package [21,22].

2. Method and computational details

2.1. Construction of ANFO configurations

To investigate the effect of fuel oil arrangement in the AN matrix on shock properties and initiations pathways, we construct two types of ANFO configuration: layered and mixed. In both cases the ANFO structure is constructed by combining AN phase IV crystal with fuel oil (FO) inclusions composed of n-dodecane ($C_{12}H_{26}$) molecules. The crystal structure of AN phase IV is orthorhombic (P4/mmb) with two $NH_4NO_3$ molecules in the unit cell and lattice constants $a = 5.65$ Å, $b = 5.28$ Å, and $c = 4.91$ Å. For layered ANFO, a thick slab of $6 \times 6 \times 7$ unit cells of AN and a thin slab of FO containing 17 $C_{12}H_{26}$ molecules are relaxed separately at 300 K to zero pressure. The two slabs are then juxtaposed in a periodic cell followed by another relaxation. The AN/FO interface is oriented normal to the [100] direction of the AN crystal. The layered ANFO structure contains 6.68 wt % fuel oil, with a density of 1.52 g/cm$^3$. A snapshot of the final equilibrated layered ANFO structure is shown in figure 1a. For mixed ANFO, a periodic supercell of $8 \times 8 \times 8$ unit cells of AN is created. Fuel oil is represented by 32 $C_{12}H_{26}$ molecules arranged in a cubic array. The molecules are added by first removing sets of three $NH_4NO_3$ groups and then inserting a $C_{12}H_{26}$ molecule into the resultant cavity in the all-trans conformation and oriented in the [100] direction of the AN crystal. The resultant structure is then relaxed to zero pressure at 300 K, giving a final mixed ANFO structure with density of 1.51 g/cm$^3$ and 6.82 wt % fuel oil. A snapshot of the final equilibrated mixed ANFO structure is shown in figure 1b.

![Figure 1.](image-url) (a) Layered ANFO (b) Mixed ANFO

Figure 1. (a) Layered and (b) mixed ANFO configurations viewed along the [010] direction of the AN crystal. For clarity, only the C-H bonds are shown for fuel oil molecules (n-dodecane, $C_{12}H_{26}$). In both cases the systems are equilibrated at 300 K and zero pressure. The periodic cell dimensions along [100], [010], and [001] are (41.5 Å, 31.4 Å, 33.6 Å) and (45.8 Å, 50.6 Å, 36.8 Å) respectively.
2.2. Shock simulation techniques

Shock properties of pure AN and ANFO mixtures, in particular the shock velocity-particle velocity ($U_S - U_P$) of principle Hugoniot states, are estimated using two different shock simulation techniques: MSST [20] and explicit NEMD simulations. For shock simulations utilizing the MSST technique, starting with an uncompressed supercell of AN or ANFO, an MD simulation is performed in which the volume and energy is adjusted to take the system to a thermodynamic state that satisfies the Rankine-Hugoniot jump conditions for conservation of mass, momentum, and energy, given a steady-state shock velocity ($U_S$) of 6-10 km/s [23, 24] under uniaxial compression. Size of AN supercell is $6 \times 6 \times 7$ unit cells of phase IV, and sizes of ANFO supercells are as described in the previous section. In explicit NEMD simulations, the atoms in an equilibrated slab of AN or ANFO are assigned an additional particle velocity $U_P$ of 4 km/s along the desired crystal direction ([100], [010] and [001]), colliding it against a reflective boundary, which mimics impact with an infinite impedance stationary wall. The properties of the resultant shock wave are estimated by averaging the properties of atoms in thin slices of the slab at successive times. The AN and ANFO initial structures in NEMD simulations are constructed by replicating the previously described supercells 8 times in the shock direction.

3. Results and discussions

3.1. Hugoniot states of pure AN and layered/mixed ANFO

To validate the overall computational approach of using ReaxFF to describe the shock properties of pure AN and ANFO mixtures, the shock velocity-particle velocity ($U_S - U_P$) Hugoniot states from NEMD and MSST are compared with that from available experiments [10–13]. Plotted in figures 2a, 2b, and 2c are $U_S - U_P$ Hugoniot states of pure AN, layered ANFO, and mixed ANFO mixtures, respectively. The numerical values of the slopes and intercepts of the approximate linear $U_S - U_P$ relationships are presented in table 1. For pure AN, figure 2a, the $U_S - U_P$ Hugoniot states from MSST and NEMD shock techniques agree very well, not only with each other but also with experimental data [10–13].

|                | Pure AN                          | Layered ANFO | Mixed ANFO          |
|----------------|----------------------------------|--------------|---------------------|
|                | Experiment | MSST [100] | MSST [010] | MSST [001] | Experiment | MSST [100] | MSST [010] | MSST [001] | Experiment | MSST [100] | MSST [010] | MSST [001] |
| $C_0$ [km/s]   | 2.20 [10], 1.80 [11], 2.13 [12], 3.10 [13] | 3.55 | 3.28 | 3.32          | –           | 3.00 | 2.97 | 2.96          | –           | 2.92 | 2.98 | 2.94 |
| $s$ [-]        | 1.96 [10], 1.80 [11], 1.82 [12], 1.60 [13] | 1.50 | 1.57 | 1.56          | –           | 1.56 | 1.57 | 1.58          | –           | 1.58 | 1.57 | 1.59 |
other, but also with experiments [10–13]. Similar levels of agreement between MSST and NEMD are observed for layered and mixed ANFO mixtures as shown in figures 2b and 2c. These principal Hugoniot states indicate that the ReaxFF force field and the MSST and NEMD techniques employed in this work provide reasonable descriptions of AN/ANFO crystals under shock compression.

![Figure 2](image-url)  
**Figure 2.** Shock velocity-particle velocity ($U_S - U_P$) Hugoniot states of (a) pure AN, (b) layered ANFO, and (c) mixed ANFO structures obtained from MSST (red, green, and blue symbols) and NEMD (magenta, cyan, and brown symbols) simulations using ReaxFF compared to available experiments (dashed lines).

3.2. Evolution of temperature during shock

Having validated the computational approach in this work, we now study the pure AN, layered ANFO, and mixed ANFO structures shocked along the [100], [010], and [001] directions via the MSST shock technique. We choose a steady-state shock velocity of 9 km/s, because at lower shock velocities no reactions were observed within the 80 ps duration of the simulations. The temperature evolution for the [010] shock direction is illustrated in figure 3. The abrupt temperature rise within the first 2 ps is due to shock compression and mechanical deformation. The second rise in temperature from 10 ps to 35 ps is due to exothermic reactions, particularly the formation of H$_2$O and N$_2$. Significant differences among the three structures are observed during this stage, and this can be attributed to the differing fueling conditions. Pure AN is underfueled and hence exhibits the lowest temperature rise. Mixed ANFO has the largest AN/FO surface area and therefore exhibits the largest temperature rise. Layered ANFO falls in between pure AN and mixed ANFO. After 80 ps, since both layered and mixed ANFO mixtures have almost the same fueling concentration, both ANFO mixtures achieve the same final temperature, while pure AN has a lower final temperature.
3.3. Shock-induced initiation of chemical reactions

Shock-induced chemical reactions initiate by endothermic dissociation of NH$_4$NO$_3$ into NH$_3$ and HNO$_3$. For the case of ANFO configurations initial reactions include the breaking of $n$-dodecane molecules into smaller hydrocarbons. Subsequent reactions involving the dissociation of nitric acid (HNO$_3$) take over, forming NO$_2$, H$_2$O, and NO$_3^-$/NH$_3$. Final products H$_2$O and N$_2$ form by reaction between NH$_3$ and NO$_2$. Illustrated in figures 4a, 4b, and 4c are the evolution of NO$_2$, H$_2$O, and N$_2$ molecules, respectively. Examining the formation of these molecular species, mixed ANFO has the fastest reaction rate that is due to the largest AN/FO surface area. Layered and mixed ANFO mixtures yield approximately the same H$_2$O concentration since both have the same amount of fuel oil. For pure AN there is not enough H to convert all oxygen atoms to H$_2$O, hence the final H$_2$O concentration is much lower. For N$_2$ molecules similar concentrations are found for all three structures, indicating that fuel oil has little effect on the formation of N$_2$. The carbon atoms in the fuel oil molecules form relatively small amounts of CO, CO$_2$, and small hydrocarbons.

We also observe a phase separation between H$_2$O and N$_2$ that has been seen previously [25–28]. Shown in figure 5 is a final snapshot of the layered ANFO shocked along the [010] direction with a steady-state shock velocity of 9 km/s after 80 ps. After approximately 10 ps, H$_2$O and N$_2$ start to form, and after approximately 50 ps, H$_2$O and N$_2$ start to separate into two phases. Carbon-containing molecules are found mostly in the N$_2$ phase due to hydrophobicity. It is also observed that for all three AN/ANFO structures shocked along all three directions, the two phases relax to a planar lamellar arrangement oriented perpendicular to one of the two principle lateral axes. This is driven by interfacial area minimization. The uncompressed simulation cell has roughly the same dimension in all three directions, but after compression it is considerably shorter in the shock direction.

3.4. Large-scale explicit NEMD shock simulation

Illustrated in figure 6 are a sequence of snapshots of a shockwave propagating through an AN crystal (phase IV) that contains a 10 nm spherical void filled with C$_{12}$H$_{26}$ molecules simulated using the NEMD shock technique. The system dimension is 24 × 17 × 17 nm and contains a total of 790,000 atoms with 4.4 wt% fuel oil. The impact velocity is 3 km/s, which is below the initiation threshold, and the impact direction is along [100]. At the instant of maximum compression (3 ps), the system is compressed to 64 % of its original volume and the average temperature rises from 300 K to 1850 K. Some chemical reactions are observed: approximately 25 % of NH$_4$NO$_3$ molecules are dissociated, 8 % of fuel oil molecules are reacted or broken into smaller hydrocarbons, around 0.5 % (relative to original number of NH$_4$NO$_3$) of NO$_2$ molecules are found in the system, and only 0.06 % of H$_2$O molecules are observed. Plotted in figure 7 is the temperature profile of the system as functions of length along the [100] direction and
Figure 4. Evolution of (a) NO$_2$, (b) H$_2$O and (c) N$_2$ species from MSST simulations for a steady state shock velocity of 9 km/s along the [010] direction: pure AN (red), layered ANFO (green), and mixed ANFO (blue).

Figure 5. Phase separation of H$_2$O (red and gray atoms) and N$_2$ (blue atoms) after 80 ps MSST simulation in layered ANFO. The steady state shock velocity is 9 km/s along the [010] direction of the AN crystal. The viewing direction is along [001]; the [010] shock direction is horizontal.

radial distance from the centerline of the void. Uncompressed AN crystal near the free surface at the bottom right remains at 300 K, while shocked AN crystal has increased in temperature to approximately 1500 K (green regions). The spherical region at the center, which is where the fuel oil was before shock compression, develops into a hotspot with temperatures higher than 2000 K (yellow, orange, and red regions). The highest temperatures of approximately 3000 K (red region) occur in the spherical shell containing the ammonium nitrate and fuel oil interface. This can be attributed both to the interface acting as a heterogeneity in the system and the fact
Figure 6. Snapshots of shockwave propagating through an AN containing a 10 nm void filled with C\textsubscript{12}H\textsubscript{26} fuel oil at (a) 0.7 ps, (b) 1.7 ps, (c) 2.7 ps, and (d) 3.0 ps after the impact.

Figure 7. Temperature profile around the developed hotspot at 3.0 ps after impact. Interface region between AN and fuel oil has the highest temperature.

that ammonium nitrate and fuel oil molecules undergo strongly exothermic chemical reactions in this region. This indicates that the presence of a void filled with fuel oil enhances overall chemical reactivity and increases sensitivity.
4. Conclusions
We have investigated shock properties of pure ammonium nitrate (AN) and layered and mixed ammonium nitrate fuel oil (ANFO) mixtures by characterizing their Hugoniot states. We utilized two different simulation techniques: Multi-scale Shock Technique (MSST), and non-equilibrium molecular dynamics (NEMD). Good agreement was obtained between both simulation methods and experimental measurements of Hugoniot states. Shock simulations of pure AN and two different ANFO configurations were performed using MSST. We found that the mixed ANFO configuration is the most reactive while pure AN is the least reactive. A phase separation of reaction products (H$_2$O and N$_2$) was observed for strong shock with all AN and ANFO configurations. A large-scale NEMD sub-threshold shock of AN crystal with a 10 nm void filled with 4.4 wt% fuel oil molecules was performed. We observed the formation of a hotspot centered on the fuel oil inclusion, with the highest temperatures occurring at the interface between AN and fuel oil molecules. Results indicate that chemical reactivity of AN is enhanced by the presence of a void filled with fuel oil.

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