

Transport in aluminized RDX under shock compression explored using molecular dynamics simulations

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Abstract. Shock response of energetic materials is controlled by a combination of mechanical response, thermal, transport, and chemical properties. How these properties interplay in condensed-phase energetic materials is of fundamental interest for improving predictive capabilities. Due to unknown nature of chemistry during the evolution and growth of high-temperature regions within the energetic material (so called hot spots), the connection between reactive and unreactive equations of state contain a high degree of empiricism. In particular, chemistry in materials with high degree of heterogeneity such as aluminized HE is of interest. In order to identify shock compression states and transport properties in high-pressure/temperature (HP-HT) conditions, we use molecular dynamics (MD) simulations in conjunction with the multi-scale shock technique (MSST). Mean square displacement calculations enabled us to track the diffusivity of stable gas products. Among decomposition products, H₂O and CO₂ are found to be the dominant diffusing species under compression conditions. Heat transport and diffusion rates in decomposed RDX are compared and the comparison shows that around 2000 K, transport can be a major contribution during propagation of the reaction front.

1. Introduction

The behavior of high explosives (HE) under extreme conditions (high pressure and temperature) is of interest for a wide range of both civilian and military applications. Insight into the response, initiation and energy dissipation mechanisms of such materials under dynamic loading and compression conditions is necessary. The material properties and response under extreme conditions can be determined through shock experiments. The state of condensed phase materials are often difficult to measure experimentally in real time because of complexity of measuring a large change in pressures (up to hundreds of GPa) and temperatures (thousands of kelvin) within a short period of time (nanoseconds to microseconds) with available instrumentation. In addition, interesting behavior, such as chemistry behind a shock front, occurs at extremely short time and length scales (nanoscale), which sometimes may pose problems in characterizing the materials using experimental capabilities. Atomistic molecular dynamics (MD) simulations have emerged as an alternative recourse to obtain information in order to develop improved macroscopic models of explosives reactivity.

The shock response of a material can be described by its Hugoniot, which is the locus of thermodynamic states accessible by shock loading from a given initial condition. This calculation can be performed through a variety of methods, such as quantum mechanical theories (wave function-based methods and density functional theory) and classical atomistic simulation methods, such as MD

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simulations. Metals are added to explosives and propellants to increase the heat of combustion. Aluminum, in particular, is commonly used because it has a high energy density. To optimize performance and safety of aluminized explosives, it is necessary to characterize and understand the role of aluminum in the explosive mixture. In experiments performed by Glumac et al. [1], AlO have been identified as species in the detonation mixtures indicating mixing of Al in early stages. However, how aluminum enters the reactive mixture is still a highly debated topic. In this work, we use MD simulations to model the behavior of RDX under shock loading conditions. In addition, we use an embedding reactivity scheme that permits us to approach the formation of stable products under conditions of a steady shock. In addition, we introduce AlO in the decomposition product to identify how a reactive mixing of aluminum species can potentially alter the reacted equation of state (EOS). In fact, introduction of Al will bring the fully reacted mixture to a highly non-ideal state which probably cannot be treated as CJ detonation. In addition, the preliminary results, presented in this paper, our thermal and shock simulations allow us to (a) incorporate and consider the γ -phase of RDX, (b) identify temperature and pressure compression state, and (c) calculate transport properties including AlO and identify the dominant diffusing species among the stable detonation products at several conditions for both pure and aluminized RDX composites.

2. Simulation Details

The nonreactive, fully flexible molecular potential developed by Smith et al. [2] was employed for all of the MD simulations. Non-bonded interactions are modeled using the Lennard-Jones potential, with parameters for RDX taken from Thompson et al. [3], and Coulomb interactions with fixed partial charges on the nuclei. In our calculations, the simulation box consists of $7 \times 3 \times 3$ unit cells of RDX, which contains 504 molecules (10584 atoms). All simulations described below were performed using the LAMMPS [4,5] code. NVT and NVE simulations were performed using integration time steps of 0.2 fs. Long-range electrostatic interactions were calculated using the PPPM method [6] and all C-H bonds were constrained to equilibrium length using the SHAKE algorithm. The accuracy threshold for forces computed using the k-space solver was set to 10^{-6} . MD simulations of uniaxial shock compression along the [100] direction were carried out over a range of shock pressures using the Multi-Scaled Shock Technique (MSST) of Reed et al. [7] as implemented in the LAMMPS Code. In the MSST simulation methodology the computational cell follows a Lagrangian point through the shock wave. This is accomplished by time-evolving equations of motion for the atoms and volume of the computational cell to constrain the stress in the propagation direction to the Rayleigh line and the energy of the system to the Hugoniot energy condition [8]. For a given shock speed, these two relations describe a steady planar shock wave within continuum theory.

3. Results

3.1. Hugoniot Curves

In order to compute the Hugoniot curves of RDX, four different systems were built. The first system, which describes the unreacted α -RDX, consists of a computational cell that is $92.274 \text{ \AA} \times 34.722 \text{ \AA} \times 32.127 \text{ \AA}$ in size. This corresponds to the ambient density of 1.80 g/cm^3 . The system to simulate the fully reactive RDX, consists of the H_2O , NO , CO_2 , N_2 , CO , and NH_3 gas products in a computational cell with the same dimensions. The amount of each gas product in the cell was calculated in order to keep the mass balance with respect to the unreacted system. Finally, to simulate the γ -RDX phase of RDX, we used the reported structure and unit cell parameters of Cumming et al. [9] to build a $7 \times 3 \times 3$ cell that is $87.955 \text{ \AA} \times 28.4307 \text{ \AA} \times 32.7891 \text{ \AA}$ in size. This corresponds to an initial density of 2.26 g/cm^3 . The corresponding cell for the fully reactive system was built by filling up the same cell with the above gas products. Once the Hugoniot have been calculated from MD simulations, the C-J points can be determined. In order to do this, the simulations results are fitted to the following function, which expresses the evolution of pressure as a function of the compression volume.

$$P(x) = ae^{-bx} + cx^{-d} \quad (1)$$

with $x = \frac{V}{V_0}$ and C-J points were obtained where x satisfies:

$$\frac{ae^{-bx} + cx^{-d}}{1-x} = abe^{-bx} + dcx^{-(d+1)} \quad (2)$$

The computed Hugoniot curves for both unreacted and fully reacted α - and γ -RDX are displayed in figure 1, where our calculated C-J points (denoted by purple star on the plot) is compared with the experimental value. As shown in the figure, there is a significant difference between the calculated C-J pressure, 26 GPa, using the α -RDX cell parameters and the reported value of 34.7 GPa. [10] Clearly, the calculated C-J pressure is underestimated and its corresponding specific volume of 0.84 is overestimated. This translates into an overestimated detonation velocity of 9493.5 m/s for RDX. Figure 1 includes also the experimental data of Ollinger et al. [11] for α -RDX (maroon star) and the data of Oswald et al. [12] for α -RDX (blue plus) and γ -RDX (green cross).

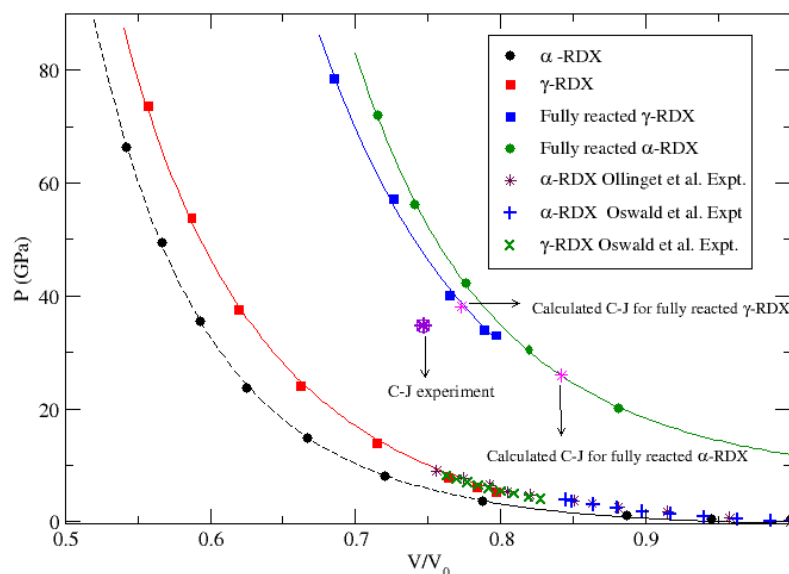


Figure 1. Calculated Hugoniot curves for α - and γ -RDX compared with experiments (α -RDX, Ref. 11 and 12. γ -RDX Ref. 12).

According to the experimental results shown in the figure, there is a deviation of the calculated α -RDX Hugoniot from the experiment for specific volumes smaller than 0.9. In the case of γ -RDX, both calculated and experiments agreed well as far as pressure versus specific volume is concerned. Finally, we also carried out compression simulations using the Buckingham potential instead. The results show that the Buckingham potential brings, to a small degree, the α -RDX Hugoniot to higher pressures compared to the one obtained using the L-J potential. For γ -RDX, both potentials compare fairly well for pressures below 15 GPa, which are more relevant when compared to existing experimental data. A more detailed quantitative analysis comparing these two pairwise potentials for RDX compression simulations will be the subject of future research. Motivated by the recent work of Gupta et al. [13,14], where the important role that the γ -phase of RDX plays at pressure and temperature conditions relevant to shock loading were demonstrated, we also incorporated this phase into our shock

compression simulations. The MD simulation results for the unreacted system of this phase are shown in the figure by the filled red squares and the corresponding fit to equation (1) is shown by the red trace. The first point of the unreacted γ -phase curve, at 5.2 GPa and 0.79 V/V₀, was calibrated using the experimental results of Davidson et al. [15] The experimental pressure could be reproduced reasonably well by a tuned L-J potential between the intermolecular O...O, O...N, O...C, and O...H interactions. In this tune L-J potential, the strength of the attractive dispersion interactions was augmented. The fully reactive Hugoniot (blue squares) and the fit (blue trace) shows that by considering the γ -phase, it brings indeed the calculated C-J pressure very close to the experimental value, as shown in the figure. Using both the C-J pressure and specific volume for this phase, a detonation velocity for 8650.2 m/s was obtained, which agrees well with the reported value of 8750 m/s [16].

3.2. Diffusion of Detonation Products

Detonation products diffusion coefficients are important parameters indicative of the mobility of each species involved. The higher the diffusivity (of one substance with respect to another), the faster they diffuse into each other. Thus, the quantification of detonation products diffusion helps in understanding the role of speciation in diffusion, which in turn, offers insights to diffusive transport at specific temperature and pressure conditions. Thus, it is believed to be an important parameter to be derived from the MD simulations. At the molecular level, the diffusion coefficient can be calculated using the well-known Einstein relation: $D = \frac{1}{2n} \lim_{\tau \rightarrow \infty} \frac{d\langle l^2 \rangle}{d\tau}$ where $\langle l^2 \rangle = \langle |r(t) - r(t + \tau)|^2 \rangle$ is the mean-square displacement of a diffusing molecule averaged over all molecules of interest and all time intervals of length τ . $r(t)$ denotes the position of a diffusing molecule at time t , and n is the dimensionality of the system in which diffusion occurs.

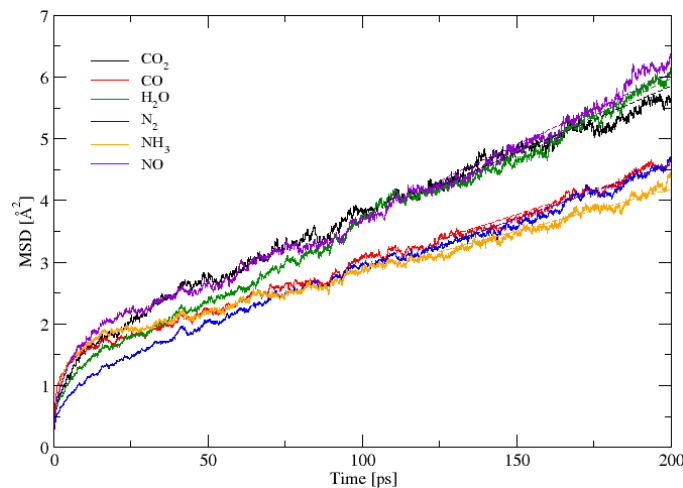


Figure 2. MSD of detonation products at 300 K.

Figure 2 shows the mean square displacements (MSD) obtained from the MD simulations for the six detonation products considered. One can observe that there is a group of products with a larger MSD, namely NO, H₂O, and CO₂. NH₃, CO, and N₂ are predicted to diffuse slower. To quantify the diffusivity of each product, we then calculated the diffusion coefficient as the slope $\frac{d\langle l^2 \rangle}{d\tau}$ from $t = 125$ - to 200-ps. The results show that the faster diffusing species is H₂O with a diffusion constant of $4.04 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and the slowest one is NH₃ with $2.25 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. In general the diffusivity order is H₂O > NO > CO₂ > N₂ > CO > NH₃ at 300 K. We also calculated diffusion coefficients for the same species at higher temperatures of 1000 and 2000 K. At these higher temperatures, the diffusivity of all detonation products is very close to each other. Nonetheless, one can see that H₂O is still the dominant

diffusing species followed by NO, CO, N₂, CO₂, and NH₃ at the highest temperature considered, 2000 K. The calculated diffusion coefficients at the three different temperatures considered are compiled in table 1.

Table 1. Detonation products diffusion coefficients calculated from MD simulations.

Detonation Product	Diffusion Coefficient [m ² s ⁻¹]		
	300 K	1000 K	2000 K
H ₂ O	4.04×10 ⁻¹¹	4.16×10 ⁻⁹	1.42×10 ⁻⁸
NO	3.86×10 ⁻¹¹	4.03×10 ⁻⁹	1.35×10 ⁻⁸
CO ₂	3.62×10 ⁻¹¹	3.49×10 ⁻⁹	1.09×10 ⁻⁸
CO	2.67×10 ⁻¹¹	3.47×10 ⁻⁹	1.26×10 ⁻⁸
N ₂	2.96×10 ⁻¹¹	3.18×10 ⁻⁹	1.20×10 ⁻⁸
NH ₃	2.25×10 ⁻¹¹	3.27×10 ⁻⁹	1.02×10 ⁻⁸

In order to obtain information about the diffusivity of the detonation products under compression conditions, two calculations were carried out at 10 and 20 GPa. The MSD of the products is reduced approximately by 40% from the non-compression case (figure 2) and up to ~ 50% for 20 GPa case. In general, the calculated MSD at these compression conditions predict very close diffusivities for the detonation products with the following order at the highest compression of 20 GPa: CO₂ ≈ H₂O ≈ NO > N₂ ≈ CO ≈ NH₃. Finally, we also calculated the MSD for the aluminized RDX detonation products by including H₂ and AlO. In this case, H₂ is the dominant diffusing species and that AlO is the slowest one at both 1000 and 2000 K. In summary, the current MSD results that H₂O and CO₂ are the dominant diffusing species make them as potential oxidizers for aluminum in early reaction zones. This is in line with recent experimental studies [1] which demonstrated that the oxidation of aluminum in aluminized explosives is robust in anaerobic (i.e. reaction with H₂O and CO₂) conditions. In addition, the calculated slow diffusion of the AlO shows that the role of Al will be limited in the growth of hot spot and majority of Al will likely participate in post-detonation combustion. We are also pursuing quantum mechanical simulations of creation of AlO species by abstraction of O from RDX and potentially leading to different branching ratios for the decomposition reactions compared to pure RDX based explosives.

Finally, we want to address the crystal RDX thermal diffusion by comparing it to the gas products diffusion. First, we gathered the magnitude of thermal diffusion of the RDX by considering its thermal diffusivity, D_T . We calculated it using the expression of Shelling et al. [17]: $D_T = k / C_v$, where C_v is the volumetric heat capacity, which is calculated using $C_v = 3rk_B$ as discussed by Schelling et al., and k is the thermal conductivity of the material. By following this procedure for RDX for $r = 0.103 \text{ atoms } \text{\AA}^{-3}$, leads to a $C_v = 4267290 \text{ J m}^{-3} \text{ K}^{-1}$. Now using $0.307 \text{ W K}^{-1} \text{ m}^{-1}$ (for a cell length very close to the one used in this study) for k as estimated by Rice et al. [18] at 300 K, the calculated thermal diffusivity is $D_T = 5.46 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. Second, we now use the average value from our previously calculated diffusion coefficients at 300 K for the detonation products listed in table 2, which is $D = 3.23 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. Comparing these two values, one can see that thermal diffusivity is much faster than species diffusion at 300 K. In general, with increasing temperature thermal conductivity, k , decreases and species diffusion increases. As an example, the average diffusion coefficient at 2000 K from table 2 is $D = 1.23 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. Thus, at high temperature detonation conditions a competitive environment for these two properties is expected for the propagation of the decomposition fronts.

4. Conclusions

We performed shock compression MD simulations using the MSST method and first-principles calculations of RDX and Al/RDX molecular systems. From the MD simulations we calculated unreacted and fully reactive Hugoniot for both α - and γ -RDX phases. From these results, we observed

that in theoretical modeling of RDX under shock loading conditions it is very important to include the γ -phase, as its inclusion improved the predicted C-J pressure. Our calculated diffusion coefficients for the RDX detonation products under both temperature and compression conditions show that H_2O , CO_2 , and NO are the dominant diffusing species and may have a lead role in blast driving reactions. This observation is in agreement with recent experimental observations, where oxidation of aluminum in aluminized explosives is robust in anaerobic environments (aluminum reacting with H_2O and CO_2). Nevertheless, the slow diffusion of the early formed AlO in the reaction zone might be a contributing factor to the delay aluminum oxidation reactions upon detonation.

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