COMPUTATIONAL MODELING OF ENERGETIC MATERIALS UNDER IMPACT AND SHOCK COMPRESSION

by

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ABBREVIATIONS

- HE high explosives
- EM energetic material
- HMX cyclotetramethylene tetranitramine $(C_4H_8N_8O_8)$
- PBX polymer bonded explosives
- MD molecular dynamics
- FEM finite element method
- EOS equation of state
- RO random orientation
- SO1 single orientation 1
- SO2 single orientation 2
- RO+F random orientation and fracture
- SO1+F single orientation 1 and fracture
- SO2+F single orientation 2 and fracture

ABSTRACT

Understanding the fundamental physics involved in the high strain rate deformation of high explosives (HE) is critical for developing more efficient, reliable, and safer energetic materials. When HE are impacted at high velocities, several thermo-mechanical processes are activated, which are responsible for the ignition of these materials. These processes occur at different time and length scales, some of them inaccessible by experimentation. Therefore, computational modeling is an excellent alternative to study multiscale phenomena responsible for the ignition and initiation of HE. This thesis aims to develop a continuum model of β -HMX to study the anisotropic behavior of HE at the mesoscale, including fracture evolution and plastic deformation. This thesis focus on three types of simulations. First, we investigate dynamic fracture and hotspot formation in β -HMX particles embedded in Sylgard binder undergoing high strain rate compression and harmonic excitation. We use the phase field damage model (PFDM) to simulate dynamic fracture. Also, we implement a thermal model to capture temperature increase due to fracture dissipation and friction at both cracks and debonded HMX/Sylgard interface. In our simulations, we observe that crack patterns are strongly dominated by initial defects such as pre-existing cracks and interface debonding. Regions with initial debonding between HMX particles and the polymer are critical sites where cracks nucleate and propagate. Heating due to friction generates in these regions too and caused the formation of critical hotspots. We also run simulations of a β -HMX particle under high-frequency harmonic excitation. As expected, higher frequencies and larger amplitudes lead to an increase in the damage growth rate. The simulations suggest that the intensity of the thermal localization can be controlled more readily by modifying the bonding properties between the particle and the binder rather than reducing the content of bulk defects in the particle.

Second, we present simulations of shock compression in β -HMX single crystals. For this purpose, we implemented a constitutive model that simulates the elastoplastic anisotropic response of this type of material. The continuum model includes a rate-dependent crystal plasticity model and the Mie-Grüneisen equation of state to obtain the pressure due to shock. Temperature evolves in the material due to plastic dissipation, shock, and thermoelastic coupling. The model is calibrated with non-reactive atomistic simulations to make sure the model obeys the Rankine-Hugoniot jump conditions. We compare finite element (FE) and molecular dynamic (MD) simulations to study the formation of hot spots during the collapse of nano-size void in a β -HMX energetic crystal. The FE simulations captured the transition from viscoelastic collapse for relatively weak shocks to a hydrodynamic regime for strong shocks. The overall temperature distributions and the rate of pore collapse are similar to MD simulations. We observe that the void collapse rate and temperature field are strongly dependent on the plasticity model, and we quantify these effects. We also studied the collapse of a micron size void in HMX impacted at different crystal orientations and impact velocities. The simulation results of void collapse are in good agreement with a gas gun void collapse experiment. While the void size and crystal orientation do not affect the area ratio rate, they strongly affect the void collapse regime and temperature. Also, increased plastic activity when the crystal is impacted on the plane (110) renders higher temperature fields.

Finally, we studied shock compression and dynamic fracture in polycrystalline HMX using the same model implemented for shocks in single crystals. The goal of this study is to understand the role of crystal anisotropy and how it affects other hotspot formation mechanisms such as frictional heating. To simulate fracture, we used a phase field damage model implemented for large deformations. We first perform simulations of sustained shocks in polycrystalline HMX, where the grains are perfectly bonded to understand the effect of plastic deformation and hotspot formation due to plastic heating. Then, we simulate shocks in polycrystalline HMX with dynamic fracture. Simulations capture fracture evolution and frictional heating at cracks. In the polycrystalline case, we study heat generation due to shock and plastic deformation. A heterogeneous temperature field forms when the shock wave travels in the material. Temperature increases more in crystals that showed a higher magnitude of accumulated slip γ_p . When weak grain boundaries are included in the simulations, frictional heating becomes the dominant hotspot formation mechanism. As the crystals' interfaces break and crack surface sliding occurs, temperature increases due to friction at cracks. Hotspots tend to form at cracks oriented 45° from the shock direction. For this case, crystal anisotropy does not play an important role in temperature generation due to plastic dissipation. However, the random orientation of the crystals creates heterogeneous deformation and stress fields that cause the formation of a higher number of hotspots than the case where all the grains are oriented in the same direction.

1. CHAPTER 1: INTRODUCTION

1.1 Motivation

When selecting an energetic material (EM) to be used as a propellant, both good detonation performance and low sensitivity are required. An EM is highly sensitive if detonation can occur easily due to stimuli such as impact, shock, friction, etc., [1]. Usually, high impact sensitivity is accompanied by good detonation performance described by the large heat of detonation. For this reason, to ensure safety during handling and transportation operations, the heat of detonation of explosive materials has to be maintained below a particular threshold. An excellent material candidate to be used as solid propellants are high explosive (HE) molecular crystals. HE are powerful solid materials; they have high density and large heat of detonation [1]. However, they are moderately sensitive to detonation due to their material defect content, and their mechanical response is very anisotropic [2]. HE are the main constituents of polymer-bonded explosives (PBX), which are used as gun propellants [3].

Despite the extensive research done in the field, it is still challenging to predict with very high fidelity both the performance and safety characteristics of HE when subjected to mechanical stimuli such as impact, friction, and shock. This is due to the multiscale nature, both in time and space, of HE's reactions when subjected to extreme conditions. Typically, HE are designed to initiate when compressed at very high or shock pressures. However, HE's shock response is greatly affected by their microstructure, particularly the presence of material defects, which can give rise to solid-phase transformations and chemical reactions that cause early ignition and initiation of the HE. The understanding of this phenomena requires in-depth knowledge in areas such as shock physics, crystallography, damage mechanics, and chemistry [4].

At Purdue University, as part of the Multidisciplinary University Research Initiative (MURI), we are interested in studying the dynamic response of a particular class of HE crystal known as β -cyclotetramethylene tetranitramine (β -HMX), which is used in PBX for-

mulations. To do so, we are working together with experimentalists and numerical modelers to study PBX from the atomic scale to the macro scale. At the macro and micro scale, experimental techniques such as gas gun and kolsky bar experiments [5]–[7] have been successfully used to characterize the damage response of energetic crystals under low and high strain rates. However, these experiments sometimes can not capture phenomena happening at the micro and lower length scales, especially when HE are shocked. Furthermore, in-situ measurements of temperature in HE crystals during compression are still challenging. Molecular dynamics (MD) simulations of energetic crystals have also been used to study the transition of viscoplastic to hydrodynamic void collapse under shock compression [8]–[10], but limited to a minimal length and time scales. Therefore, a continuum model and simulations are needed to study better the anisotropic behavior of HE and PBX at the mesoscale, including fracture evolution and plastic deformation. This mode can be calibrated with MD results and validated with experiments. The model will also help us connect phenomena happening from the nanoscale to the mesoscale to understand the ignition of HE better.

1.2 Introduction to high explosives (HE)

1.2.1 Polymer bonded explosives (PBX)

Polymer bonded explosives (PBX) are a type of composite energetic material that consist of HE crystals, e.g., cyclotetramethylene tetranitramine (HMX), cyclotrimethylene trinitramine (RDX), pentaerythritol tetranitrate (PETN), triaminotrinitrobenzene (TATB), embedded in a polymeric binder, e.g., thermoplastic polyurethane (TPU), hydroxyl-terminated polybutadiene (HTPB), polydimethylsiloxane (PDMS). The microstructure of PBX 9501 is shown in Figure 1.1. Formulations of PBX contain up to 90-95 % by weight of HE and 2.5-10 % of binder [1]. The HE crystals are moderately insensitive and the binder is usually an elastomer whose function is to make the explosive less prone to accidental detonation. During manufacturing, PBX are highly compressed, inducing the formation of macroscopic defects such as cracks and debonding at binder-crystal interfaces. Besides, HE crystals are highly anisotropic and contain a large density of defects such as pores, dislocations, shear bands, and twin boundaries [11], [12]. Despite their low sensitivity at atmospheric conditions, PBX may ignite and detonate under relatively low shock/impact velocities (20 -100 m/s) [13]. This situation occurs due to the formation of regions of localized thermal energy termed as hotspots. Material defects may be preferential sites for the nucleation of hotspots.



Figure 1.1. Microstructure of PBX 9501 composed of 95% β -HMX crystals and 2.5% estane binder [12].

1.2.2 Crystalline structure and properties of HMX

HMX or cyclotetramethylene tetranitramine (C₄H₈N₈O₈) is a type of high energy molecular crystal commonly used in PBX. HMX can be found in four polymorphic forms, δ , γ , α , and β . The β phase is the most stable one at room temperature [14] and has a melting point around 552 K. β -HMX crystals are obtained by evaporation of solvents such as acetone at 293 K [15].They crystallize into a monoclinic structure with lattice constants of a=6.54 Å, b = 11.05 Å, c = 8.70 Å and β =102.3 °, in the space group $P2_1/n$ [16]. The unit cell for this type of crystal is formed of two (2) molecules as shown in Figure 1.2.

 β -HMX crystals have been characterized under quasi-static loading [14], [17]. When they are deformed at low-stress rates, these crystals tend to be very brittle and fracture under low-stress magnitudes. In crystallography studies, it was observed that this type of crystals have cleavage on the plane (011), and twinning with mirror planes on the (101). Twinning allows HMX crystals to withstand large deformations before fracturing [17]. Additionally, ten (10) slip systems have been identified for β -HMX from indentation experiments, and MD simulations [18].



Figure 1.2. Unit cell representation of the monoclinic β -HMX crystal in the $P2_1/n$ space group.

1.3 Hotspots in HE

Before a HE material detonates, it has to undergo a series of sequential events termed as ignition (start of deflagration), deflagration growth (burning), a transition from deflagration to detonation (DDT), initiation (onset of detonation), and propagation of detonation. When HE are dynamically loaded, regions of localized thermal energy known as hot spots are formed. Hotspots with high-enough temperatures trigger the chemical decomposition and reaction of the HE. Suppose the hotspot's thermal energy due to exothermic chemistry is generated at a higher rate than the energy dissipated due to heat conduction and endothermic reactions. In that case, the hot spot will grow in size and temperature [19], [20]. The growth and agglomeration of these "critical" hotspots can lead to a steady-state deflagration, as well as the build-up to a detonation wave [21]–[23].

Tarver et al. [19] studied the criticality of hotspots in HE. According to Tarver, for β -HMX, critical cylindrical hotspots usually have dimensions of 0.1 to 10 μ m, durations of 10^{-5} to 10^{-3} s, and temperatures greater than 700 K. In the literature, several hot spot formation mechanism in EM have been studied including collapsed of gas cavities, void collapse (viscous and hydrodynamic), shear banding, localized plastic dissipation, and friction at cracks [13]. In this work, the focus is on hotspot formation due to void collapse, frictional heating, and plastic dissipation due to crystallographic slip. Void collapse is known to result in dominant hotspots and plays a crucial role in the initiation of chemical reactions, and eventually, a transition to detonation [22]. During the collapse of voids, hotspots are generated due to various processes that depend on void geometry, size, and shock strength. For strong shock conditions, the formation of ejecta gas molecules leads to hotspot formation [24]. This mechanism is usually referred to as hydrodynamic void collapse, characterized by the formation of a jet with a velocity greater than the material velocity [25], [26]. In the case of weaker shocks, dissipation due to localized plastic deformation around the void plays a critical role [27]–[29]. Heating due to plastic dissipation can increase the temperature in HE hundreds of degrees up to their melting point.

Due to the high content of pre-existing defects in HE such as cracks, frictional heating is of significant concern. It has been related to being the cause of accidental detonation during handling and transportation of HE. Frictional heating occurs due to both contact crystal to crystal in PBX and sliding between cracks surfaces during unstable crack growth in HE. According to Dienes et al. [30] frictional heating at closed cracks can cause detonation of HE. If the melting temperature is reached in a hot spot at a crack, burning gases will start to be released locally, pressurizing the crack. Consequently, if inertial effects inhibit crack growth, the pressure will keep building up inside the cracks, and some adjacent critical hotspots may coalesce. Therefore, the reaction zone is expanded, and finally, detonation occurs. The synergistic effect of frictional heating acting together with other mechanisms at the same time may increase the probability of accidental detonation [13].

1.4 Dynamic fracture in HE

HE crystals are very brittle materials. From nanoindentation experiments, the fracture energy of β -HMX has been estimated to be around 0.06 J/m² [17] which is less than the fracture energy of a crystal of sucrose [31]. Under quasi-static load, HE fracture behavior can be described by Griffith's energy balance. Griffith states that the total energy of a system containing a crack is the sum of the energy absorbed to grow a crack, known as the fracture energy, plus the elastic energy released due to unloading happening around the crack's vicinity [32]. Therefore, crack propagation occurs if the available energy reaches a critical value. For a plate with an initial crack of length a, the critical tensile stress for crack propagation σ_f can be obtained from the following expression:

$$\sigma_f = \sqrt{\frac{EG_c}{\pi a}} \tag{1.1}$$

E is the Young's modulus of the material, and G_c is usually referred to as the critical energy release rate, or fracture toughness of the material and its units are J/m^2 , which is the energy needed to propagate a crack by a unit area. For a brittle material, the fracture energy can be calculated as $G_c = 2\gamma$, where γ is the surface energy. Suppose a plastic zone of considerable size is formed at the crack tip in quasi-brittle materials. In that case, the plastic work has to be added to the surface energy $G_c = 2\gamma + w_p$ to match experimental observations [33]. A fracture test usually determines this quantity of G_c .

If the same system with a crack is loaded at a significant rate, the system will acquire kinetic energy and becomes dynamic. In this case, the effect of inertial forces becomes important, and the Griffith theory no longer applies. In dynamic fracture, crack growth is unstable, and crack tip velocity is limited by the speed of sonic waves inside the material. A good estimate of the crack terminal velocity is $c_T \approx 0.38c_1$ where $c_1 = (E/\rho)^{1/2}$ is the longitudinal speed of sound [34]. Another approximation of the terminal velocity is the shear wave velocity $c_2 = (\mu/\rho)^{1/2}$ where μ is the shear modulus of the materials. It has been observed in brittle materials that when cracks propagate at velocities above $0.6c_2$ they tend to bifurcate. This phenomenon is known as crack branching and according to Yoffe [35], in an isotropic and linear elastic material, branching is produced due to the stress field's dynamical nature. Crack branching can be beneficial since it enhances the fracture toughness (G_c) by preventing cracks from reaching their terminal velocity of c_T .

The fracture strength of brittle materials σ_f also differs in tension and compression. Cracks propagate under compressive load if stresses become tensile at heterogeneities in the material such as micro cracks, twins, and micro-voids, or stress wave reflections at crack surfaces/boundaries. The fracture strength of brittle materials under compression exhibits pressure and strain rate dependency. Brittle materials can sustain considerable plastic deformation when compressed at high pressures [36]. If the loading conditions allow creating high shear stresses, crystallographic slip due to dislocations might occur, causing plastic deformation at the crack tip. Therefore, stresses are relaxed at a more significant area leading to an increase in the energy release rate G_c . β -HMX crystals can develop twinning, which allows them to deform plastically before fracturing [17]. In this case, crack propagation may start when dislocations are stopped by obstacles such as grain boundaries or dislocation pile-ups, causing the stress to increase locally to a magnitude greater than the fracture strength. Another way to inhibit fracture is by applying lateral or confining pressure. Wiegand et al. [37] studied the effect of confinement in a cylindrical PBX subjected to axial compressive load for hydrostatic confining pressures in the range of 0.1 and 138 MPa. In their experiments, they observed a transition from brittle to ductile for pressures over 7 MPa. The compressive strength increased linearly with the strain rate log at constant pressure. Furthermore, their PBX samples' compressive strength also increased linearly with confinement pressure at a constant strain rate. Surface cracking was observed for low pressures, whereas for higher pressures, plastic deformation inhibited fracture. Brittle to ductile transition in brittle crystals is also affected by stain rate [38]. A faster strain rate likely induces brittle fracture. As strain rate increases, ductility decreases since dislocations do not have enough time nucleate and propagate [39].

1.5 Shock waves in energetic materials

When solids are compressed at very large stress amplitudes, much greater than the its yield strength, solids start to behave like compressible fluids. This fluid-like behavior is a consequence of the generation and motion of defects such as dislocations formed at the wavefront where high plastic deformation occurs [40]. This compression generates a strong non-thermal internal pressure caused by repulsive forces between atoms and thermal pressure due to electron-phonon scattering. Under these conditions, shock waves form. A shock wave is defined as a discontinuity in pressure, temperature, and density across a layer whose thickness tends to zero [40], [41]. Let's consider a material initially unshocked with constant pressure P_0 , density ρ_0 , velocity U_0 and temperature T_1 , which is impacted applying a piston velocity on its left boundary U_p (see Figure 1.3). The material is subjected to very high pressure, causing a shock wave that propagates at a velocity of U_s . In the shocked region, the material flow properties are P_1 , ρ_1 , U_1 and T_1 . The shock can be described by applying the conservation of mass, momentum, and energy equations from an initial state at rest P_0 , E_0 , and ρ_0 to a highly compressed state P_1 , E_1 , and ρ_1 , where E is the internal energy per unit mass. Assuming that the material is initially at rest $(U_0=0, P_0=0)$ and the particle velocity in the shock region is $U_1 = U_p$, we can obtain the Rankine - Hugoniot jump conditions:

$$\rho_0 U_s = \rho_1 (U_s - U_p) \tag{1.2}$$

$$P_1 - P_0 = \rho_0 U_s U_p \tag{1.3}$$

$$P_1 U_p = \rho_0 U_s (E_1 - E_0 + \frac{U_p^2}{2})$$
(1.4)

If all the initial conditions ahead of the shock are known, four remaining unknowns $(P_1, \rho_1, U_s, \text{ and } E_1)$ are left, and only three equations. Therefore, a fourth equation is needed, known as the equation of state (EOS), which relates the shock and particle velocities using a polynomial function as follows:



Figure 1.3. Schematic of shock wave traveling in a solid.

$$U_s = c_0 + s_1 U_p + s_2 U_p^2 + \dots (1.5)$$

where c_0 is the bulk sound speed and s_i where i = 0, 1, 2, ..., n are the fitting coefficients. For some materials that do not undergo a phase transition, the EOS is a linear function of the following form:

$$U_s = c_0 + sU_p \tag{1.6}$$

Combining the EOS and the energy balance equation, we can obtain an expression of the pressure P = f(v) where v is the specific volume. This relationship is called the hugoniot equation, as shown in Figure 1.4. The hugoniot may be formed by two or more segments representing phase transformations or transition from elastic to the plastic regime. In the P-v plane the hugoniot can be expressed as:

$$P = c_0^2 (v_0 - v_1) [v_0 - s(v_0 - v_1)]^{-2}$$
(1.7)

In literature, it is common to see experimental results of P-v states for shock-compressed solids that represent the locus of all shocked states rather than a continuous loading path. The straight line that connects the unshocked and shocked states (see Figure 1.4) is known as the Rayleigh line, and its equation is given by:

$$U_s = v_0 [(P - P_0) / (v_0 - v_1)]^{1/2}$$
(1.8)



Figure 1.4. P-v diagram for a shock showing hugoniot and isentrope curves, and rayleigh line.

The Rayleigh line slope is proportional to the square of the shock wave velocity of U_s . The hugoniot defines all possible final shock states attainable by a single shock process. For HE, usually, two kinds of hugoniots are reported: the unreacted and reacted curve. Using experimental results of the hugoniot and theoretical background, one can obtain a mathematical expression for the EOS. For solids, the Mie-Grüneisen (MG) EOS [42], [43] is used extensively, from which the shock pressure can be calculated:

$$P_{eos} = \Gamma \rho_0 C_v \left(T_0 - T \right) \left(\frac{v_0}{v} \right) + \frac{K_0 \eta}{\left(1 - s\eta \right)^2} \left[\frac{\Gamma}{2} \left(\frac{v_0}{v} - 1 \right) - 1 \right]$$
(1.9)

where Γ is the Grüneisen parameter, C_v is the specific heat, v_0/v is the specific volume ratio, K_0 is the reference bulk modulus, s is the slope of the Hugoniot equation, and $\eta = 1 - v/v_0$. A comparison of the Mie-Gruneise (MG) EOS with MD and experimental results is shown in Figure 1.5. Another commonly used EOS for HE is the Birch-Murnaghan (BM) EOS, which has been calibrated for β -HMX under shock [42]:

$$P = \frac{3}{2}K_0 \left[\left(\frac{v_0}{v}\right)^{5/3} - \left(\frac{v_0}{v}\right)^{7/3} \right] \left[1 + \frac{3}{4}(K_{T0} - 4) \left[\left(\frac{v_0}{v}\right)^{2/3} - 1 \right] \right]$$
(1.10)

where K_{T0} is the bulk modulus pressure derivative. For β -HMX crystals, the BM EOS has shown to be a good fit with experimental results for non-hydrostatic compression below 10 GPa and hydrostatic compression below 27 GPa. This is because chemical reactions and phase transformation can occur above this pressure value, so the constants c_0 and s from the hugoniot might change [44].

When a material is shocked at a pressure larger than the yield point referred to as the hugoniot elastic limit (HEL), a two-step wave profile is generated composed of a leading elastic wave and an inelastic wave that propagates at a lower velocity. This wave split is hardly seen in experiments. The shape of the wave profile is affected by strain hardening, or visco-plastic flow in the material [45]. Since plastic deformation is rate dependent, the HEL determined from the magnitude of the elastic precursor is not unique and depends on the experimental technique.

1.6 Computational modeling of HE

Before discussing computational models of HE, it is important to understand what types of commercial codes are available to study shock waves in solids, usually referred to as hydrocodes. Throughout history, both Lagrangian and Eulerian finite element codes, such as ALE3D, have been extensively used to simulate the impact and shock waves in energetic materials [18], [25], [46]–[48]. In Lagrangian codes, the mesh is embedded in the material, and under the application of a load, the mesh distorts, making it easy to track the history of variables. In contrast, Eulerian codes make use of a fixed mesh in which mass flows through. However, neither Lagrangian nor Eulerian frameworks have proven to be superior to each other. For instance, Lagrangian codes require complex subroutines to handle nonlinear problems such as the collapse of a void, friction and sliding, making shock simulations



Figure 1.5. Comparison equations of state (EOS) for β -HMX in the $U_s - U_p$ plane, obtained experimentally [5], [7], and from non-reactive MD simulations (courtesy of Professor Strachan's group).

computationally intensive. Eulerian codes are preferred for large deformations, but calculating stresses and frictional effects at interfaces can be challenging without adding Lagrangian features.

For β -HMX, there are significant theoretical studies in the literature that use both Lagrangian and Eulerian methods [18], [25], [49]. These studies have focused on modeling the collapse of voids and the different hotspot generation mechanisms involved in the process. Barton et al. [18] used a continuum Lagrangian-Eulerian code and a dislocation based crystal plasticity model to study the collapse of a 10 μ m diameter void in a β -HMX single-crystal impacted at $U_p = 1$ km/s. The model was calibrated using gas gun experiments and molecular dynamics simulations. They observed that plastic shear localization led to the formation of hotspots due to shear-banding. Later on, Austin et al. [49] extended this model to account for chemical reactions. In their results, they noticed that significant temperature localization occurred due to both shear banding and mass reactivity inside the shear bands. Their results concluded that shear banding happened as a result of viscoplasticity capture in the model.

Rai and Udaykumar [25] used an Eulerian solver to study the collapse of cylindrical voids. β -HMX was modeled using a rate-independent perfectly plastic material model where thermal softening was also included. In their simulations, they observed transition from plasticity-dominated collapse to jet formation at shock pressures over P = 6.89 GPa. Keyhani et al. [50] simulated a microstructure of PBX consisting of HMX and estane, impacted with piston velocities up to 1.2 km/s. Their model included a viscoplastic and viscoelastic material model for the HE and binder, a cohesive zone fracture model, and heat generation due to plastic dissipation and frictional heating. They observed that the importance of each mechanism on the formation of hotspots depends on the load conditions; plastic dissipation is more significant as the piston velocity increases, but frictional heating, even though it is reduced with piston velocity, is more localized and can also play an essential role at high piston velocities. They concluded that crystals with low yield strength and low friction coefficient are less sensitive to form hotspots. Similarly, Springer et al. [47] presented eulerian void collapse simulations in which they were able to predict the formation of shear bands at low shock pressures. They concluded that strain-rate hardening, captured by the Johnson and Cook plasticity model they used, is the main reason for the growth of shear bands.

Other Lagrangian constitutive models have been proposed in the literature to study RDX under shock [46], [51]–[53]. These models have been helpful to simulate the elastic-plastic split of waves generated during shock compression experiments by using dislocation-based crystal plasticity models. For instance, De et al. [52] developed an anisotropic elastoplastic thermomechanical model to study α -RDX under shock. The model incorporated dislocation motion and generation. Simulations showed crystal orientation dependency in the shock pressure and particle velocity due to crystalline slip activity. Luscher et al. [46] proposed a dislocation-based crystal plasticity model for α -RDX to simulate weak shocks and study transition from drag-limited to thermally activated dislocation motion due to shock loading. Their simulations of shocks at different crystallographic orientations showed good agreement with plate impact experimental results in RDX. MD simulations have also been used to inform continuum mesoscale models of HE [54]– [56]. For instance, Wood et al. [55] used large scale MD simulations to study different hot spot formation mechanisms during the collapse of a void in an hexanitrostilbene (HNS) crystal. The continuum model included a strain rate dependent strength material using Sandia's CTH code [48]. The authors were able to model the transition from viscoplastic to hydrodynamic void collapse as the shock pressure increases. Furthermore, they observed that the pore collapse rate increased significantly with void size, especially at low shock pressures. A similar study by Zhao et al. [56] compares one to one MD and Eulerian continuum simulations of pore collapse in TATB, highlighting the need for sophisticated continuum models to capture with high fidelity the anisotropic response of HE. Kroonblawd and Austin [57] in a recent study, employed MD and mesoscale simulations to capture melting and liquid viscosity as a function of temperature and pressure in HMX under shock loading. They observed that at high shock pressures melting is suppressed, and consequently, hotspots are formed due to plastic dissipation.

HE crystals under shock have also been study at the molecular scale. Jaramillo et al. [8] used MD simulations to characterize α -RDX shocked in the direction [100]. As the piston velocity is increased from 0.4 to 1.0 km/s they observed a transition from dislocation glide to nano-scale shear banding. Nanoshear bands in RDX were also observed in MD simulations by Cawkwell et al. [9] when the crystal was impacted normal to the plane (100) at 1.0 km/s. Furthermore MD simulations have been used to obtain the thermomechanical properties of energetic crystals. Sewell et al. [2] reported the full elasticity tensor and bulk modulus for β -HMX and other HMX polymorphs at room temperature obtained from MD using the Smith - Bharadwaj force field [58]. MD results were in good agreement with experimental data. Recently Mathew and Sewell [59] also reported the elastic moduli for β -HMX for pressures between 0.1 and 30 GPa.

1.7 Experimental techniques to study HE

The mechanical response of single β -HMX crystals under shock has been characterized under both quasi-static and high strain rate loading. Experimental techniques such as splitHopkinson/Kolsky bar, gas gun, and laser-driven flyer impact, along with diagnostic tools such as laser interferometry and high-speed x-ray phase-contrast imaging (PCI), have been used to obtain particle velocities and in-situ images of the deformation field in HE [5]–[7]. Techniques such as the Velocity Interferometer System for Any Reflector (VISAR) [60] have allowed researchers to obtain shock profile measurements in HE at time resolutions around 1 ns and shock pressures up to 40 GPa. Tests such as gas gun experiments have been useful to estimate dynamic stresses at strain rates around 10^3 - 10^4 . Additionally, researchers have obtained experimentally in real-time images of hotspots in HMX and PBX at the micro and nano time resolution, using techniques such as thermal microscopy and optical pyrometry [61], [62].

In the quasi-static regime, Rae et al. [63] obtained the stress-strain response of β -HMX crystals compressed along the [001] direction and on the (110) plane. When loading on the (110) orientation, they observed a more elasto-plastic response due to the activation of twinning/slip on the (101) plane in the [101] direction. Palmer et al. [17] also observed the formation of elastic twinning bands on the {101}-planes during nano-indentation experiments. On the dynamic loading side, J.J Dick et al. [7] performed gas gun experiments and obtained the particle velocity in HMX crystals shocked at 1.5 and 2.4 GPa on three different planes: (110), (011), and (010), all in the $P2_1/n$ space group. Their gas gun experiments captured the propagation of both an elastic wave followed by a plastic wave for piston velocities $U_p \approx 0.3$ km/s. Additionally, they reported the existence of two different hugoniots, one for shocks normal to the (010)-plane and the other for the orientations (110) and (011). Interestingly, they also observed that the elastic precursor's magnitude changed with crystal orientation being the highest for the shocks on the (010) plane. They claimed that shocks normal to the plane (010) do not activate the primary slip or twin systems, so the crystal response is more brittle.

Kerschen et al.[6] obtained the evolution of the damage field during impact in single β -HMX crystals embedded in Sylgard binder using high-speed x-ray phase contrast imaging (PCI). They observed cracking inside HMX crystals and debonding at the crystal/binder

interfaces when samples were impacted at velocities between 0.2 and 0.3 km/s. Volume expansion, cracking, and debonding were only observed at an impact velocity of 0.445 km/s, which seems to result from chemical reactions that originated at the cracks. Fracture in β -HMX has also been studied using flyer impact experiments. Zaug et al. [5] was able to characterize the fracture response of single β -HMX crystals shocked at pressures up to 40 GPa and time resolution around 10 ps, using laser-driven flyer plate impact and ultrafast time-domain interferometry (TDI). The crystals were shocked normal to the planes (010) and (110) in the $P2_1/n$ space group. After shocking the crystals, they observed more damage for the crystal orientation (010) than the (110)-oriented crystals. For the (110) orientation, cracks were observed to form parallel in a specific direction. The cracks observed for the (110) orientation had this pattern due to slip and twinning activation before brittle fracture occurred. Furthermore, for the (010) crystal orientation, they observed the time-dependent response of the crystals going from an elastic-dominated response to volume reduction due to phase transformation and endothermic reactions when the shock pressure was above 27 GPa.

Laser-driven flyer plate impact has also been used to study the dynamic response of HE. Using this technique, Basset and Dlott [64] studied hotspot temperature evolution in shocked ultrafine HMX powder impacted at a velocity of 4.3 km/s. They measured temperature spikes up to 6700 K. They concluded that the magnitude and duration of the spikes depended not only on the explosive chemistry but also on the shock wave's interaction with the sample microstructure. Recently Belinda et al. [62] using the same experimental technique, observed hot spots on the nanoscale in shocked single HMX crystals embedded in polyurethane binder and PBX. The temperature of the hotspots was captured during laser-driven flyer shock loading. In the single HMX crystal configuration, hotspots formed primarily at the edges and corners of the crystals. In the PBX samples, the hot pots formed at voids and crystal junctions had higher temperatures and lasted longer.

Ultrasonic excitation experiments have been used to study the nucleation of hotspots in specimens with discrete, energetic crystals [61], [65], [66]. Mares et al. [67] used an infrared camera to obtain the temperature field in samples with particles excited at high-frequencies.

They recorded a maximum temperature rise of 5 °C on the surface of samples containing HMX particles after 2 s of excitation at 215 kHz. The temperature rise in samples containing AP particles was in the range 6 °C to 10 °C while for sugar particles, the temperature rise was up to 5 °C. Additional AP and HMX samples were excited for a longer time, and some samples ignited within 15 s. You et al. [61] studied hotspot formation in polymer samples containing sucrose, PBX, RDX, and NaCl particles subjected to excitation frequencies of 20 kHz with amplitudes from 27 μ m to 44 μ m. To investigate the effect of particle/binder adhesion, some particles were coated with polyethylene glycol (PEG) and others with Teflon. The authors report the formation of hotspots with a temperature of 600 K in sucrose crystals coated with PEG after 60 ms. In contrast, no increase in temperature is observed in the polymer's bulk or sucrose particles without coating. Similar results are reported for samples containing PBX, RDX, and ammonium nitrate particles. Hotspots are also observed in NaCl inclusions coated with PEG and Teflon. In all the experiments, no cracks are observed in the particles, but smoothing of the surfaces is reported in particles coated with PEG. Chen et al. [66] also studied hotspot generation by ultrasonic excitation in RDX crystals embedded in a PDMS binder. After 110 ms of excitation, they observed chemical decomposition of some of the RDX crystals, indicating a local temperature increase of at least 500 K. Furthermore, localized heating was observed in the polymer regions adjacent to the particle edges that spread to the crystals' bulk. Recently, using ultrasonic periodic excitation, Roberts et al. [68] observed phase transition in β -HMX crystals decomposed into the non-centrosymmetric phase δ -HMX. This indicates that the crystals reached temperatures over 463 K at which δ -phase transitions in HMX occurs.

1.8 Research goal and outline

This project aims to develop a thermodynamically consistent continuum model that captures the anisotropic response of single β -HMX crystals and polycrystalline HMX subjected to extreme conditions. The model should simulate fracture evolution and plastic deformation in β -HMX crystals compressed at high strain rates and capture different heat localization mechanisms such as frictional heating, plastic dissipation, and shock heating, which are known to cause the formation of hotspots. Plastic deformation is modeled using a ratedependent phenomenological single crystal plasticity model. Fracture evolution is simulated using an anisotropic phase field damage model (PFDM) for large deformations. Information obtained from molecular dynamics (MD) simulations is also used to inform and calibrate the continuum model.

Chapter 1 was dedicated to discussing relevant literature to build the continuum model, including an introduction to HE, dynamic fracture in HE, a summary of shock wave physics in solids, and a review of computational models and experimental techniques used by other authors to study the response of HE crystals under shock. The structure of the remaining parts of this thesis is as follows: Chapter 2 describes the theory of the continuum model used to simulate dynamic fracture in β -HMX using the phased field damage model (PFDM). Additionally, it includes a temperate model that simulates hotspot formation due to frictional heating and crack propagation. Simulations of single HMX particles embedded in Sylgard and impacted at non-shock velocities are shown and compared with experiments. Chapter 3 presents the theory to simulate shock compression in single crystals. The theory includes a crystal plasticity model for β -HMX single crystals, an equation of state (EOS), a proposed PFDM for large deformations, and a temperature model that simulates temperate increase due to shock compression, plastic dissipation, thermo-elasticity, and friction. The continuum model is used to simulate void collapse during shock compression at the nano and meso scales. In Chapter 4, we used the continuum model developed in the previous chapter to study shock compression in polycrystalline HMX and understand the role of crystal anisotropy. Finally, a summary of this work and its impact in the field of energetic materials is discussed in Chapter 5.
2. CHAPTER 2: FRACTURE AND HOT-SPOT FORMATION AT CRACKS IN HEs

Preamble

Sections 2.3, 2.4, and 2.5 of this chapter have been published in the following papers:

C. A. Duarte, N. Grilli, and M. Koslowski. "Effect of initial damage variability on hotspot nucleation in energetic materials". Journal of Applied Physics 124, 025104 (2018); URL: https://doi.org/10.1063/1.5030656.

N. Grilli, C. A. Duarte, and M. Koslowski. "Dynamic fracture and hot-spot modeling in energetic composites". Journal of Applied Physics 123, 065101 (2018); URL: https://doi.org/10.1063/1.5009297.

C. A. Duarte, R. Kohler, and M. Koslowski. "Dynamic fracture and frictional heating due to periodic excitation in energetic materials". Journal of Applied Physics 124, 165109 (2018); URI: https://doi.org/10.1063/1.5048723.

2.1 Introduction

As it was discussed in Chapter 1, PBXs are very sensitive to mechanical and thermal insults that can lead to accidental ignition and detonation [69], [70]. Experimental results in PBXs show that initial defects, such as pre-existing cracks and voids in the energetic particles and debonding at particle-matrix interfaces, affect the PBX's sensitivity by reducing the time-to-ignition and the threshold pressure for initiation [17], [71], [72]. The link between defects and ignition times has been studied parametrically with numerical models [30], [49], [73]. In the energetic materials community, there is an agreement that initial defects in PBX's heterogeneous microstructure are responsible for forming hot-spots. Still, this process is poorly understood as it involves complex thermo-chemical and fluid, and structural interactions.

Hot-spot formation is a mesoscale phenomenon, and therefore, several numerical computational studies in energetic materials incorporate the heterogeneity of the material using statistical approaches. One example is the statistical crack mechanics (SCRAM) developed by Dienes et al. [30]. Their results indicate that frictional heating can increase the temperature up to 700 K around a shear crack, leading to hot-spot nucleation. However, the SCRAM does not resolve the propagation and interaction of single cracks. Moreover, it does not take into account friction on the particle-binder interface. Akiki and Menon [74] developed a hot spot-model that can represent heating due to void collapse, friction, and plasticity. In their work, the formulation is evaluated in HMX with heating due to void collapse with viscoplastic deformation. Their result showed that larger voids make the material more sensitive. For void with a size larger than 5 μ m, the energy released from the collapse reaches an asymptotic value. The energy contribution from voids smaller than 1 μ m can be neglected when larger voids are present.

Mesoscale simulations that explicitly include individual defects at the particle level help understand some of the unique mechanisms that lead to the hot-spots formation. Most of the work is focused on void collapse using atomistic [10], [55],and Eulerian formulations [25],[49], [75], [76]. The Eulerian simulations include thermal and chemical reactions, and the mechanical response is limited to plastic deformation and does not take into account fracture. Udaykumar et al. [75], [76] performed mesoscale simulations to parametrically study the effect of microstructure (voids and cracks) on the initiation threshold due to viscous and plastic work heating. The microstructure is implicitly considered by introducing randomly distributed voids and cracks of different shapes and sizes. Their simulations show that long cracks lead to ignition and initiation; however, samples with smaller voids did not ignite for the same shock load. In particular, the analysis of individual elongated cracks shows that a critical crack orientation angle, between 30° and 50° with respect to the incident shock, is the most sensitive to ignition. All these mesoscale studies focus on the high energy material. In contrast, the work of Barua et al. [77], [78], establishes that particle-binder interfaces have a critical role in the formation of hot-spots. Their simulations show that higher volume fractions of particles correspond to increased heating and a lower threshold for fracture initiation. These simulations do not consider the initial microstructure (voids or microcracks) of the individual particles [79].

To study the effect of initial defects on the formation of hot-spots in PBX, a predictive model that includes initial defects inside the particles and at particle-polymer interfaces is developed in this work. Finite element simulations of dynamic fracture and thermal transport are performed to investigate the response of β -HMX particles embedded in a Sylgard binder under compression, with impact velocities in the range of 10 m/s to 400 m/s. A parametric study of the effect of the initial cracks and impact velocity on damage is performed. The impact of surface defects, such as steps and debonding, is also studied. A comparison with experimental images of β -HMX particles in Sylgard, made with microsecond acquisition rate, during gas gun experiments [6] has been used to calibrate parameters needed for HMX. The heat transport equation is solved in the simulations to find the temperature field due to surface friction at cracks using a phase-field damage model (PFDM). The temperature obtained in the simulations at impact velocity 400 m/s is sufficient to ignite the β -HMX particle based on Tarver's criterion [19].

2.2 Computational models

This section explains the mathematical framework developed to simulate fracture and hot-spot formation due to frictional heating at cracks in a β -HMX crystal subjected to impact. In this work, fracture is modeled by solving the motion and phase field damage equations, and frictional heating is included in the energy balance equation as a heat flux boundary condition at the crack surface.

2.2.1 The phase field damage model (PFDM)

Consider a body with volume Ω , external boundary $\partial \Omega$, and containing a fractured surface Γ as shown in Figure 2.1. The displacement of $\mathbf{x} \in \Omega$ is given by $\mathbf{u}(\mathbf{x}, t)$. Assuming small deformations, the infinitesimal strain tensor $\boldsymbol{\varepsilon}(\mathbf{x}, t)$ in indicial notation is defined as:

$$\varepsilon_{\rm ij} = \frac{1}{2} \left(\frac{\partial u_{\rm i}}{\partial x_{\rm j}} + \frac{\partial u_{\rm j}}{\partial x_{\rm i}} \right) \tag{2.1}$$

For isotropic and linear elastic materials, the elastic strain energy density is given by the following expression:

$$\psi_{\rm e} = \frac{1}{2}\lambda \left(\varepsilon_{kk}\right)^2 + \mu \varepsilon_{\rm ij} \varepsilon_{\rm ij} \tag{2.2}$$

where λ and μ are the Lamé constants. Griffith's theory of brittle fracture [32] states that the potential energy of any system is given by the sum of the elastic strain energy and the fracture energy as follows:

$$W_{pot}(\boldsymbol{\varepsilon}, \Gamma) = W_{e}(\boldsymbol{\varepsilon}) + W_{f} = \int_{\Omega} \psi_{e}(\boldsymbol{\varepsilon}) d\mathbf{x} + \int_{\Gamma} G_{c} ds \qquad (2.3)$$

where G_c is known as the fracture toughness or critical energy release rate of the material. The kinetic energy is given by:

$$W_k(\dot{\mathbf{u}}) = \int_{\Omega} \rho \dot{u}_i \dot{u}_i d\mathbf{x}$$
(2.4)

Therefore, the Lagrangian of the system is defined as:

$$L(\mathbf{u}, \dot{\mathbf{u}}, \Gamma) = W_k(\dot{\mathbf{u}}) - W_{pot}(\boldsymbol{\varepsilon}(\mathbf{u}), \Gamma) = \int_{\Omega} \left[\rho \dot{u}_i \dot{u}_i - \psi_e(\boldsymbol{\varepsilon})\right] d\mathbf{x} - \int_{\Gamma} G_c ds$$
(2.5)

In the phase field approximation, a scalar variable $c(\mathbf{x}, t)$ is introduced to track the discontinuity Γ . This scalar variable represents the damaged or fractured material if $c(\mathbf{x}, t) = 1$, and material in intact status if $c(\mathbf{x}, t) = 0$. Francfort and Marigo [80] introduced this phasefield formulation of fracture, and used Griffith's energy minimization principle [32]. The phase-field damage model's main advantage is that it automatically tracks complex fracture processes such as crack initiation, crack propagation, and crack branching by evolving a continuous damage variable on a fixed mesh. Therefore, to model 3D fracture, there is no need to create complicated meshes that explicitly include the cracks. Also, no ad-hock criterion is needed since the damage evolution is described based on energetic arguments. Several quasi-static and dynamic phase field models of damage have been proposed to study brittle fracture [81]–[83], and its application has been extended to study fracture in ductile materials [84], [85], and anisotropic fracture. In the phase field approximation, the crack surface is regularized as in [86], so the fracture energy in Equation 2.3 can be written as an integral over the volume as follows:

$$\int_{\Gamma} G_c ds \approx \int_{\Omega} \gamma(c, \boldsymbol{\nabla} c) d\mathbf{x} = \int_{\Omega} G_c \left(\frac{1}{2l_0} c^2 + \frac{l_0}{2} \left| \boldsymbol{\nabla} c \right|^2 \right) d\mathbf{x}$$
(2.6)

where $\gamma(c, \nabla c)$ is the crack density, and l_0 is a length scale parameter that characterizes the width of the damaged zone. When $l_0 \to 0$ the diffused damage surface becomes the sharp crack surface Γ . Since fracture only occurs under tensile load, the elastic energy density functional is split into two components, $\psi_0^+(\boldsymbol{\varepsilon})$, representing the part of the strain energy density that degrades with damage, and $\psi_0^-(\boldsymbol{\varepsilon})$ the part that is not affected by damage:

$$\psi_{\mathbf{e}}(\boldsymbol{\varepsilon}, c) = \left[(1-c)^2 + k_r \right] \psi_0^+(\boldsymbol{\varepsilon}) + \psi_0^-(\boldsymbol{\varepsilon}) . \qquad (2.7)$$

In Equation 2.7, k_r is a residual stiffness that ensures the positive definiteness of $\psi_{\rm e}(\boldsymbol{\varepsilon}, c)$. The form of the free energy split depends on the material response. The most common splits of the strain energy density are known as the strain spectral decompositio [82] and volumetric-deviatoric strain decomposition [81]. Using the spectral decomposition of the strain, the components of the strain energy can be written as follows:

$$\psi_0^+(\boldsymbol{\varepsilon}) = \frac{\lambda}{2} \langle \operatorname{tr}(\boldsymbol{\varepsilon}) \rangle^2 + \mu \operatorname{tr}\left(\left(\boldsymbol{\varepsilon}^+\right)^2\right) ,$$
 (2.8)

$$\psi_0^-(\boldsymbol{\varepsilon}) = \frac{\lambda}{2} (\operatorname{tr}(\boldsymbol{\varepsilon}) - \langle \operatorname{tr}(\boldsymbol{\varepsilon}) \rangle)^2 + \mu \operatorname{tr}\left(\left(\boldsymbol{\varepsilon}^-\right)^2\right) , \qquad (2.9)$$

where $\lambda = \frac{E\nu}{(1+\nu)(1-2\nu)}$ and $\mu = \frac{E}{2(1+\nu)}$ are Lamé's, E is the Young modulus, and ν the Poisson ratio. The operator $\langle \cdot \rangle$ is defined as $\langle x \rangle = \frac{1}{2}(x+|x|)$, and the tensors ε^+ and ε^- are:

$$\boldsymbol{\varepsilon}^{+} = \begin{bmatrix} \langle \varepsilon_1 \rangle & 0 & 0 \\ 0 & \langle \varepsilon_2 \rangle & 0 \\ 0 & 0 & \langle \varepsilon_3 \rangle \end{bmatrix}$$
(2.10)

$$\boldsymbol{\varepsilon}^{-} = \begin{bmatrix} \varepsilon_1 - \langle \varepsilon_1 \rangle & 0 & 0 \\ 0 & \varepsilon_2 - \langle \varepsilon_2 \rangle & 0 \\ 0 & 0 & \varepsilon_3 - \langle \varepsilon_3 \rangle \end{bmatrix}, \qquad (2.11)$$

where $\varepsilon_1, \varepsilon_2, \varepsilon_3$ are the principal strains. Therefore, tensile strain, which gives positive principal strains, induces damage. Propagation of mode II cracks can also be reproduced by this model because damage is induced by simple shear, in which one of the eigenvalues of the infinitesimal strain tensor is positive [82]. In order to make the model thermodynamically consistent and to prevent healing of the damage zone, the next inequality needs to be satisfied:

$$\dot{\Gamma}(c, \nabla c) = \int_{\Omega} \dot{\gamma}(c, \nabla c) d\mathbf{x} = \int_{\Omega} \delta_c \gamma \cdot \dot{c} \, d\mathbf{x} \ge 0 \,.$$
(2.12)

To satisfy Equation 2.12 the next conditions have to be enforced: $\delta_c \gamma \geq 0$ and $\dot{c} \geq 0$, where $\delta_c \gamma = \partial_c \gamma - \nabla \cdot \partial_{\nabla c} \gamma$ is the functional derivative. The Langrangian in terms of the phase field variable c is given by:

$$L(\mathbf{u}, \dot{\mathbf{u}}, c) = W_k(\dot{\mathbf{u}}) - W_{pot}(\boldsymbol{\varepsilon}(\mathbf{u}), c) = \int_{\Omega} \left[\rho \dot{u}_i \dot{u}_i - \psi_e(\boldsymbol{\varepsilon}(\mathbf{u}), c) - G_c \gamma(c, \boldsymbol{\nabla} c)\right] d\mathbf{x}$$
(2.13)

Using the Euler-Lagrange equations the balance of momentum and damage field equations are obtained:

$$\sigma_{ij,j} = \rho \ddot{u}_i , \qquad (2.14a)$$

$$\dot{c} - \frac{1}{\eta_c} \left\langle l_0 \Delta c + 2(1-c) \frac{\psi_0^+(\boldsymbol{\varepsilon})}{G_c} - \frac{c}{l_0} \right\rangle = 0 , \qquad (2.14b)$$

where:

$$\sigma_{ij} = \frac{\partial \psi_e}{\partial \varepsilon_{ij}} = \left[(1-c)^2 + k_r \right] \frac{\partial \psi_0^+}{\partial \varepsilon_{ij}} + \frac{\partial \psi_0^-}{\partial \varepsilon_{ij}} .$$
(2.15)

The inertia term in Equation 2.14a limits the crack propagation speed to the Rayleigh speed, which is around 2.67 km/s for β -HMX. The constant η_c in Equation 2.14b is a kinetic coefficient that controls the relaxation of the system towards equilibrium [82]. The Equations 2.14a and 2.14b can be written in their weak for as:

$$\int_{\Omega} \delta w_{i} \rho \ddot{u}_{i} d\mathbf{x} + \int_{\Omega} \nabla_{j} \delta w_{i} \sigma_{ij} d\mathbf{x} - \int_{\partial \Omega} \sigma_{ij} n_{j} \delta w_{i} ds = 0$$
(2.16a)

$$\int_{\Omega} \delta c \left(\dot{c} - \frac{1}{\eta_c} \left\langle l_0 \Delta c + 2(1-c) \frac{\psi_0^+(\boldsymbol{\varepsilon})}{G_c} - \frac{c}{l_0} \right\rangle \right) d\mathbf{x} = 0$$
(2.16b)

where δw_i and δc are test functions. The integrals in Equations 2.16a and 2.16b are implemented and solved numerically in the finite element software MOOSE (Multiphysics Object Oriented Simulation Environment)[87] using the backward Euler scheme.



Figure 2.1. (a) 2D representation of sharp crack Γ in a volume Ω with boundary $\partial \Omega$, and (b) diffuse crack with thickness $2l_0$ using the phase field damage model (PFDM).

2.2.1.1 Numerical examples

As mentioned before, one of the biggest advantages of the PFDM is that it allows modeling crack initiation and propagation-based only on energetic arguments without the use of any ad hoc criterion. To verify the damage model, we performed Mode I and Mode II fracture simulations on a 2D squared domain with 1 μ m side. For the mode I example, a boundary velocity of $\bar{v}_n = 0.01 \ \mu m/ns$ was applied normal to the top boundary and frictionless support is used at the bottom boundary ($u_y = 0.0$). In the Mode II example, a tangential boundary velocity of $\bar{v}_n = 0.1 \ \mu m/ns$ was applied on the top boundary, and the bottom boundary was again held fixed. Furthermore, in other to simulate crack branching, we increased the load rate for the Mode I specimen to $\bar{v}_n = 0.1 \ \mu m/ns$. The material properties and damage model parameters used in the simulations are shown in Table 2.1. In Figure 2.2 (a) and (b) simulation results for the examples of mode I and mode II fracture are presented, showing typical crack propagation patterns at angles 0° and 45°, respectively. Additionally, in Figure 2.2 (c), crack branching is obtained in the Mode I example by increasing the load rate.

Property	Value
E (GPa)	25.12
ν	0.24
$ ho~({ m kg/m^3})$	1910
$G_c \; ({ m J/m^2})$	2
$c_v (\mathrm{J}/(\mathrm{kg} \cdot \mathrm{K}))$	1576
$k (W/(m \cdot K))$	0.31
μ_f	1.0
k_r	$1\cdot 10^{-6}$
$\eta_c \; (\mathrm{s/m})$	0.1
$l_0~(\mu{ m m})$	0.4

Table 2.1. Mechanical, thermal, and phase field properties for β -HMX used in damage simulations.



Figure 2.2. Examples of damage evolution for a specimen subjected to (a) Mode I loading applying displacement $\bar{v}_n = 0.01 \ \mu m/ns$, (b) Mode II with $\bar{v}_t = 0.1 \ \mu m/ns$, and (c) Mode I at higher strain rate $\bar{v}_n = 0.1 \ \mu m/ns$ showing crack branching. Time steps $t_1 < t_2 < t_3$.

2.2.2 Hot-spot modeling

2.2.2.1 Heat equation

The conservation of energy equation in the current configuration is written as:

$$\rho \dot{\mathbf{e}} = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \boldsymbol{\nabla} \cdot \mathbf{q} + \rho r \tag{2.17}$$

The behavior of the material is defined using the next expression of the Helmholtz free energy:

$$\psi = \hat{\psi}(\boldsymbol{\varepsilon}, T, c) \tag{2.18}$$

The Helmholtz free energy can be written in terms of the internal energy and entropy as follows:

$$\psi = \mathbf{e} - T\eta \tag{2.19}$$

where η is the entropy per unit mass, and T is the temperature. Differentiating Equation 2.19 with respect to time $(\dot{\psi} = \dot{e} - \dot{T}\eta - T\dot{\eta})$ and substituting into Equation 2.17:

$$\rho\dot{\psi} = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \rho \dot{T} \eta - \rho_0 T \dot{\eta} - \boldsymbol{\nabla} \cdot \mathbf{q} + \rho r$$
(2.20)

where $\mathbf{q} = -k\boldsymbol{\nabla}T$ and k is the material thermal conductivity. Furthermore, differentiating Equation 2.18 with respect to time and applying chain rule:

$$\dot{\psi} = \frac{\partial \hat{\psi}}{\partial \varepsilon} \dot{\varepsilon} + \frac{\partial \hat{\psi}}{\partial T} \dot{T} + \frac{\partial \hat{\psi}}{\partial c} \dot{c}$$
(2.21)

The state relations as a function of the Helmholtz free energy are:

$$\boldsymbol{\sigma} = \rho \frac{\partial \hat{\psi}}{\partial \boldsymbol{\varepsilon}}, \eta = -\frac{\partial \hat{\psi}}{\partial T}, \rho c_v = T \frac{\partial \eta}{\partial T} = -T \frac{\partial^2 \hat{\psi}}{\partial^2 T}$$
(2.22)

where c_v is the specific heat. Differentiating the entropy with respect to time we have:

$$\dot{\eta} = \frac{d}{dt} \left(-\frac{\partial \hat{\psi}}{\partial T} \right) = -\frac{\partial}{\partial T} \left(\dot{\psi} \right) = -\left(\frac{\partial^2 \hat{\psi}}{\partial T \partial \boldsymbol{\varepsilon}} : \dot{\boldsymbol{\varepsilon}} + \frac{\partial^2 \hat{\psi}}{\partial^2 T} \dot{T} + \frac{\partial^2 \hat{\psi}}{\partial T \partial c} \dot{\boldsymbol{\varepsilon}} \right)$$
(2.23)

The heat equation becomes:

$$\rho c_v \dot{T} = -\frac{\partial \hat{\psi}}{\partial c} \dot{c} + T \left(\frac{\partial^2 \hat{\psi}}{\partial T \partial \boldsymbol{\varepsilon}} : \dot{\boldsymbol{\varepsilon}} + \frac{\partial^2 \hat{\psi}}{\partial T \partial c} \dot{c} \right) + \nabla \cdot k \boldsymbol{\nabla} T + \rho r$$
(2.24)

Neglecting the terms due to thermo elastic heating $\frac{\partial^2 \hat{\psi}}{\partial T \partial \varepsilon}$: $\dot{\varepsilon} = 0$, and reversible heat generation due to damage $\frac{\partial^2 \hat{\psi}}{\partial T \partial c} \dot{c} = 0$, the heat equation can be rewritten as:

$$\rho c_v \dot{T} = \nabla \cdot k \nabla T + \rho \left(r + r^c \right) \tag{2.25}$$

where $r^c = -\frac{\partial \hat{\psi}}{\partial c} \dot{c}$ is the dissipative heat generation due to fracture. The heat equation can be written in its weak form as:

$$\int_{\Omega} \rho c_v \dot{T} \delta \theta d\mathbf{x} - \int_{\Omega} \mathbf{q} \cdot \boldsymbol{\nabla} \delta \theta d\mathbf{x} + \int_{\partial \Omega_T} h \delta \theta ds - \int_{\Omega} \rho \left(r + r^c \right) \delta \theta d\mathbf{x} = 0$$
(2.26)

where $\delta\theta$ is a test function and, $h = \mathbf{q} \cdot \mathbf{n}$ is the outward heat flux through the surface $\partial\Omega_T = \partial\Omega \cup \Gamma$. The third term of Equation 2.26 is divided into two components representing the domain boundary and the cracks:

$$\int_{\partial\Omega_T} h\delta\theta ds = \int_{\partial\Omega} h^s(\mathbf{n})\delta\theta ds + \int_{\Gamma} h^c\delta\theta ds , \qquad (2.27)$$

where $h^{s}(\mathbf{n}) = -k\nabla T \cdot \mathbf{n}$ is the outward heat flux. The last term in Equation 2.27 is the heat flux generated due to frictional sliding between the crack surfaces and can be calculated from the following expression [88]–[90]:

$$h^c = -\mu_f \left\langle -t_n \right\rangle v^s , \qquad (2.28)$$

where μ_f is the friction coefficient, $t_n = \mathbf{n}_i \boldsymbol{\sigma}_{ij} \mathbf{n}_j$ is the normal component of the traction vector at the crack surface, and v^s is the magnitude of the sliding velocity between the two surfaces of the crack. The symbol $\langle \rangle$ in Equation 2.28 ensures that heat is generated only when the traction is negative, i.e. only when the cracks are closed. The sliding velocity can be obtained as $[|\mathbf{v}_i|]$ across the crack surface, which can be approximated as:

$$[|\mathbf{v}_{\mathbf{i}}|] = l_x \mathbf{v}_{\mathbf{i},\mathbf{j}} \mathbf{n}_{\mathbf{i}}^c \tag{2.29}$$

where l_x is the characteristic length that is assumed to be the crack thickness l_0 , and \mathbf{n}_j^c is the unit normal vector, pointing outwards the crack surface:

$$\boldsymbol{n}^{c} = -\boldsymbol{\nabla}c/\left|\boldsymbol{\nabla}c\right| \quad . \tag{2.30}$$

Equation 2.29 is justified by the fact that the velocity gradient is localized in the damaged region during shear deformation. This is because the strain tensor during shear deformation has one positive and one negative eigenvalue, therefore shear stiffness is degraded. The

sliding velocity is the projection of the velocity jump vector, which has magnitude $[|\mathbf{v}_i|]$, on the crack surface plane and it is given by:

$$v^{s} = \left[\delta_{ij} - n_{i}n_{j}\right] \left\|\mathbf{v}_{i}\right\| \tag{2.31}$$

Using Equation 2.28, the second term on the right hand side of Equation 2.28 can be written as:

$$\int_{\Gamma} h^c \delta\theta ds \simeq \int_{\Omega} \left(\frac{c^2}{2l_0} + \frac{l_0}{2} \left| \boldsymbol{\nabla} c \right|^2 \right) h^c \delta\theta d\mathbf{x}$$
(2.32)

2.2.2.2 Numerical examples

In this section, numerical examples are used to verify the heat generation model due to friction described in the previous subsection. For this purpose, in the following examples, the heat source due to damage propagation is neglected. Three examples corresponding to tensile, compressive, and shear loading applied on a square particle of β -HMX are discussed. Material properties and parameters used in the simulations are listed in Table 2.2. The geometry of the examples consists of a square with side length 1.0 μ m (see Figure 2.3). The domain is discretized using first-order quadrilateral elements with size h = 0.04 μ m, and the length scale parameter l_0 is taken as twice the element size, for both the compression and tension examples. For the shear loading example, the element size is taken as h= 0.02 μ m and $l_0 = 4$ h. For the tension and compression examples, Dirichlet temperature boundary conditions are set as $T^+ = 300$ K and $T^- = 400$ K on the top and bottom boundaries, respectively. For the shear loading case, temperature boundary conditions are set as $T^+=T^-$ = 293 K on both top and bottom boundaries. Zero heat flux boundary condition is used at the remaining boundaries, see Figure 2.3. The initial value of the temperature is $T_0 = 293$ K in the whole domain.

Displacement boundary conditions are applied as a ramp function $u_y^{\pm}(t) = \pm$ (2.0 · $10^{-5}\mu$ m/ns) t for both tension and compression cases on the top and bottom boundaries, as shown in Figure 2.3. For the tensile loading case, the left and right boundaries are traction

free (Figure 2.3 (a)). For the compressive loading case, the left boundary has zero horizontal displacement, while the right boundary is traction free (Figure 2.3 (b)). A notch is included in all the domains using an exponential function that corresponds to the 1D solution of the phase field evolution equation, given by:

$$c(d) = c_{max} e^{(-|d|/l_0)} , \qquad (2.33)$$

where d is the distance perpendicular to the crack and $0 < c_{max} < 1$. To account for degradation of the thermal conductivity with damage, k is expressed as a function of the damage phase field as follows:

$$k(c) = (1 - c^2)k^s + c^2k^c , \qquad (2.34)$$

where k^s is the thermal conductivity of the solid and k^c of the damaged material. In this work $k^c = 0$. This is to avoid heat conduction across open cracks.

Experimental measurements of the friction coefficient of β -HMX are rare in literature, and they are obtained only for small sliding velocities. Confinement experiments on PBX have been used to deduce indirectly a value of the friction coefficient between 0.6 and 0.7 [37]. Sliding experiments between two β -HMX crystals have shown a pressure dependence of the friction coefficient, with values between 1.0 at lower pressure and 0.6 at higher pressure [91]. Because of this uncertainty on the friction coefficient, we have used a value $\mu = 1.0$ (Table 2.1). If heat conduction is slow enough, the temperature values found in the simulations can be adapted to different friction coefficients by rescaling the temperature increase.

The damage and temperature fields for the tension example in Figure 2.3(a) are shown in Figures 2.4 (a) and (b) at two different times. The initial crack is modeled using the representation in Equation 2.33, with $c_{max} = 1.0$. For the value of the boundary velocity chosen (0.002 m/s), crack propagation under tension has taken place after 5 μ s, which corresponds to an average tensile strain of 1%. As the crack propagates, a jump discontinuity in the temperature field is observed and, due to the tensile loading, no heat sources are

Property	Binder (Sylgard 184)	Particle (β -HMX)
E (GPa)	0.159	25.12
ν	0.48	0.24
$ ho~({ m kg/m^3})$	1030	1910
$G_c \; (\mathrm{J/m^2})$	400	2
$c_v (\mathrm{J}/(\mathrm{kg} \cdot \mathrm{K}))$	1423	1576
$k^s (W/(m \cdot K))$	0.27	0.31
μ_f	1.0	1.0
k_r	$1 \cdot 10^{-6}$	$1 \cdot 10^{-6}$
$\eta_c \; ({ m s/m})$	0.1	0.1

Table 2.2. Mechanical and thermal properties for β -HMX [92] and Sylgard binder [93]–[95].



Figure 2.3. Geometry and boundary conditions of the examples. The β -HMX particle is subjected to (a) tension including a notch in the middle of the particle with $c_{max} = 0.5$, (b) compression having a through crack with $c_{max} = 1.0$, and (c) compression and shear loading with $c_{max} = 1.0$.

propagation r_c is neglected, and only crack surface friction is considered. Figure 2.4(c) shows temperature profile along the line $x = 0.5 \ \mu \text{m}$ at different time steps. It can be seen that at $t = 5.0 \ \mu \text{s}$ there is an abrupt change in temperature at $y = 0.5 \ \mu \text{m}$, which approaches the 1-D steady-state solution.

The damage and temperature fields at $t = 5.0 \ \mu s$ for the compressive case presented in Figure 2.3(a) and (b). The initial crack is modeled using the representation in Equation



Figure 2.4. (a) Damage phase field and (b) temperature field in the β -HMX particle at $t = 1.0 \ \mu s$ and 5.0 μs . (c) Temperature profile along the line x=0.5 μm (see white dashed line) at different times .

2.33, with $c_{max} = 0.5$. Damage does not evolve since the particle is subjected to compressive stress. Furthermore, heat generation due to friction is not activated since there is no sliding or relative motion between the two surfaces. After $t = 5.0 \ \mu$ s the numerical solution overlaps the analytical steady-state solution.

The shear loading example's geometry and boundary conditions are shown in Figure 2.3(c). First, the particle is compressed by $u_{y0}=0.05 \ \mu \text{m}$ until $t=0.15 \ \mu \text{s}$. After $t=0.15 \ \mu \text{s}$ a displacement boundary condition u_x is applied on the top part of the left boundary of the domain, using a linear function with $u_x = 2.0 \cdot 10^{-3} \mu \text{m/ns} (t-150 \text{ns})$. The bottom part of the left and right boundaries of the domain is fixed. There is no evolution of the damage phase field in this example. In this way, a direct comparison with the analytical solution is possible. The damage and temperature fields at $t=0.20 \ \mu \text{s}$ are shown in Figure 2.5 (c). The temperature increases along the crack due to frictional heating. High values of temperature are observed at the crack edges due to high velocity gradients.

In Figure 2.5 (d), the temperature distribution from the numerical solution is plotted at different time steps along the line $x=0.5 \ \mu$ m, from the center of the crack to the top boundary of the domain (see dashed lines). After shearing starts ($t > 0.15 \ \mu$ s), an increase in temperature is observed along the crack. As shear deformation becomes larger, the increase in temperature at the crack becomes more evident. Numerical results are compared with the 1-D analytical solution of the transient heat equation (see Equation 2.20) in a semi-infinite space, with constant surface heat flux $(-k \frac{dT}{dy} = \bar{h^c})$ at the crack line [96] and initial condition T= 293 K. The values of $\bar{h^c}$ used for each time t_i are obtained from the numerical results by integrating the heat rate per unit volume over y and taking its average value over time $(\bar{h^c} = \frac{1}{t_i - t_0} \int_{t_0}^{t_i} h^c dt)$, from the onset time of the shear deformation $t_0 = 0.15 \ \mu s$ until the time of interest t_i . Temperature profiles along the y axis obtained from the analytical solution are shown in Figure 2.5 (d) (see solid lines). The numerical results show fair agreement with the analytical 1-D solution.

2.3 Simulations of HMX particles under impact loading

2.3.1 Numerical model

The response of single HMX particles bonded to a Sylgard matrix under impact loading is studied with 2D finite element simulations with the fracture mechanics and thermal models described previously. The geometries and the velocities used in the simulations quantitatively reproduce the experiments carried out by Kerschen et al. [6]. Figure 2.6 (a) shows a representation of the samples used in the gas gun experiments, consisting of HMX particles surrounded by Sylgard. Figure 2.6 (b) shows X-ray images of the sample before and after the impact showing crack propagation and debonding between the particle and the binder.

The material properties and parameters used in the simulations are summarized in Table 2.1. It has been shown that the crack propagation depends on the value of these parameters and the mesh size. A coarse mesh, with an element size equal to l_0 , reduces the crack propagation velocity [97] and leads to an overestimation of the dissipated energy [86]. Mesh sizes from 2.5 μ m to 10 μ m were used to analyze convergence. As expected, smaller elements



Figure 2.5. (a) Damage and temperature fields of the β -HMX particle under compression at $t = 5 \ \mu$ s. (b) Temperature over the line $x = 0.5 \ \mu$ m (see white dashed line) at t = 1 and 5 μ s. (c) Damage and temperature field at $t = 0.02 \ \mu$ s in HMX particle subjected to simple shear. (b) Comparison temperature over line $x = 0.5 \ \mu$ m obtained from FE simulations (bold curves) and analytical solution (dashed curves).

lead to crack branching not observed in the simulations with element size 10 μ m. The local temperature prediction changes 10% when the element size is increased from 2.5 μ m to 10 μ m.

The crack propagation velocity is inversely proportional to η [98]. A value of the kinetic coefficient $\eta = 0.1$ s/m used in the present paper has been applied previously to the simulation of single edge notch tension specimens [83]. It has resulted in a strain rate-independent behavior for strain rates between 10^{-4} s⁻¹ and 1 s⁻¹. More simulations and experiments are needed to calibrate the value of η for HMX [97], [99]. The surface energy determined by micro indentation in HMX is 0.06 J/m^2 [17] in the {011} plane. To include the effect of plasticity under compression in HMX [94], an approximated value of the energy release rate $G_c = 2 \text{ J/m}^2$ is used here. Due to the high uncertainty in the energy release rate, the



Figure 2.6. (a) Schematic of the sample used in the gas gun experiment Kerschen et al. [6]. The β -HMX particle is embedded in Sylgard 184, and it is impacted with an impact velocity U_p . (b) X-ray image of the experiment with impact velocity of 445 m/s.

present model is simplified and does not include anisotropy in the elastic constants or the energy release rate.

2.3.2 Results

2.3.2.1 Effect of initial crack orientation

A 2D sample with 700 μm width and 500 μm height, shown in Figure 2.7, is used to study the effect of initial crack orientation on the particle damage. This domain is discretized using 56,960 second order quadrilateral elements with an average size of 2.5 μ m. Impact loading is simulated by imposing a velocity U_p in the x direction on the left surface of the sample. All boundary conditions are shown in Figure 2.7 and plane strain deformation is assumed. The HMX particle contains three initial cracks and the orientation of the central crack is set to $\theta = 0^{\circ}$, 45° and 90°. Initial cracks are represented with an exponential decaying function:

$$c(\mathbf{r}, t=0) = c_{max} e^{-\frac{|\mathbf{r}|}{l_0}}$$
, (2.35)

where **r** is the distance perpendicular to the crack line and $c_{max} = 1$. This exponential function represents a stationary crack and it is an exact time-independent solution of Equation 2.15 when external loads are not applied, i.e., $\psi_0^+(\varepsilon_{ij}) = 0$ [82].



Figure 2.7. Geometry and boundary conditions to study the dependence on crack orientation.

The evolution of the damage phase field for the different initial crack orientations is shown in Figure 2.8 for an impact velocity $U_p = 10$ m/s. The initial crack that intersects the left HMX-Sylgard interface grows in the direction of the stress wave. This compressive stress wave produces a vertical expansion of the sample. For all the initial crack configurations, damage grows in the horizontal direction in agreement with the experiments in Figure 2.6 and in reference [100]. The compressive stress wave is reflected by the HMX-Sylgard interfaces, the initial cracks, and the right boundary. When the stress wave reaches the right HMX-Sylgard interface, a reflected tensile wave initiates the crack's propagation at the right interface. This crack deflects toward the top free surface. In Figures 2.8 (a) and (b) the central crack is oriented at 0° and 45°, these cracks propagate horizontally while the vertical crack in Figure 2.8 (c) does not grow in length. In all the simulations, it is observed that large deformation gradients at the interface lead to debonding in the top part of the HMX-Sylgard interface. Branching of the cracks is also observed for higher velocities, see Figures 2.8 (b) and (c).



Figure 2.8. Time evolution of the damage at times t = 1.4, 2.2, 2.6 μ s and impact velocity $U_p = 10$ m/s with different crack orientations $\theta = 0^{\circ}$ in (a), $\theta = 45^{\circ}$ in (b) and $\theta = 90^{\circ}$ in (c). White regions in the damage field represent values c > 0.97.

2.3.2.2 Effect of the impact velocity

To study the dependence of the impact velocity on the particle damage, the geometry and boundary conditions shown in Figure 2.9 are used in this section. Boundary velocities from 10 m/s to 400 m/s, similar to the ones used in the experiments of Kerschen et al. [6] are simulated. An initial crack at 45° from the direction of the impact velocity and two horizontal initial cracks that intersect the HMX-Sylgard interface are considered. The domain is discretized using 58254 second order quadrilateral elements with an average size of 2.5 μ m.

The time evolution of the damage phase field is shown in Figure 2.10 for impact velocities $U_p = 10$, 100 and 400 m/s. The contour plot of the volumetric stress $\sigma_{vol} = \sigma_{ii}/3$ is shown in the Sylgard matrix and it displays the stress wavefront. In all the cases, the cracks grow



Figure 2.9. Geometry and boundary conditions to study damage evolution in a single particle β -HMX-Sylgard system.

in the particle, and no damage is observed in the polymer. When the impact velocity is 10 m/s, Figure 2.10 (a), a crack pattern with horizontal cracks advancing in the particle, similar to the one in Figure 2.8 is observed. When the impact velocity is increased to 100 m/s, crack branching appears (Figure 2.10 (b)) as a result of higher input energies [99], [101]. Figure 2.10 (b) also shows damage nucleation at the horizontal HMX-Sylgard interface. At an impact velocity $U_p = 400$ m/s, the localized damage at the interface is more evident and follows the stress wave propagating in the polymer. Extensive damage is observed in the particle propagating from the horizontal interface that merges with the 45° initial crack.

These simulations show crack propagation aligned along the x-axis due to the vertical expansion of the particles. This is in agreement with single-particle experiments [6] and multiple particle experiments in [100] where horizontal cracks are observed. However, other crack orientations are present in the experiments at higher impact velocities. This may indicate that pre-existing cracks may be distributed through the HMX particle and that other crack nucleation mechanisms are not captured with 2D simulations. It is also observed that the polymer's debonding and crack propagation from the particle surface towards the interior are induced by pre-existing surface defects. This takes place at a volumetric stress of 1.2 GPa for $U_p = 400$ m/s, as shown in Figure 2.10 (c). This result is in agreement with



Figure 2.10. Time evolution of the damage for impact velocity (a) $U_p = 10$ m/s, (b) $U_p = 100$ m/s, and (c) $U_p = 400$ m/s. White regions represent values of the damage field c > 0.95.

the tests by Czerski et al. [102] that show that the shock sensitivity is strongly affected by surface defects and morphology during shock tests.

2.3.2.3 Temperature field predictions

The effects of the boundary velocity and the interface damage on the temperature field are studied in this section. 2D simulations of the single-particle β -HMX-Sylgard system in Figure 2.9 are performed and compared to the same geometry with initial damage added to the interface (represented by bold black lines in Figure 2.11). Initial damage is modeled as cracks with length 50 μ m, located at the HMX-Sylgard interface, described by the decaying exponential function in Equation 2.35 with c_{max} chosen randomly between 0 and 1 for each crack. It is important to notice that the lack of data for the friction coefficient, μ , limits the temperature prediction. However, the model can be used to calculate the relative effect of initial cracks, debonding, and impact velocities.



Figure 2.11. Geometry and boundary conditions to study the temperature increase due to crack friction. The black bold segments at the HMX-Sylgard interface are initial interface cracks.

Figure 2.12 shows the temperature field for impact velocities $U_p = 100$ m/s and 400 m/s with and without initial interface damage. The only temperature source considered here is friction at cracks. Therefore, in all the simulations, temperature increases in initial cracks and cracks that developed during the simulation. As expected, the temperature reaches a larger value at higher velocity boundary conditions due to higher stresses and velocity gradients. When there is no damage debonding the HMX-Sylgard interface, the maximum temperature increase is located at the intersection of the left HMX-Sylgard interface and the initial horizontal crack. When initial debonding is included, the maximum temperature increase takes place in the same region. Furthermore, it can be observed in Figure 2.12 that the presence of interface damage augments the size of the high-temperature regions near the left side of the HMX particle. This is of importance because the increment in temperature and the size of the hot-spots determines the probability of ignition [19].



Figure 2.12. Temperature contour plots at time t = 1.1 μ s, and t =0.28 μ s for $U_p = 0.1$ and 0.4 km/s, respectively. The circles indicate the regions with the highest temperature.

Figure 2.13 shows the evolution of the temperature in the node that reaches the maximum temperature in the HMX crystal for $U_p = 10$ m/s, 100 m/s, 400 m/s. The presence of pre-existing damage at the HMX-Sylgard interface increases significantly the maximum temperature. This effect becomes more evident at impact velocity $U_p = 400$ m/s. For instance, at impact velocity $U_p = 10$ m/s, the temperature increase is $\Delta T \approx 0.3$ K, whereas for $U_p = 100$ m/s, $\Delta T \approx 103$ K, and for 400 m/s, $\Delta T \approx 900$ K. The results indicate that the synergetic effect of a debonded interface, with cracks intersecting the crystal surface, can favor the formation of hot spots.

The temperature reached for $U_p = 400$ m/s is above the melting point of HMX, which is 552 K [103], and above the transition temperature to the δ -phase [104]. However, in the present model these phenomena are not considered. In the present simulations, in which the total time considered is of the order of 1 μ s, the thermal conduction does not play an important role. The temperature field is strongly correlated to the heat source and only limited heat transfer takes place. Following Tarver's model [19], a 10 μ m hot spot, comparable to the size of the highest temperature regions (red color in Figure 2.12, is expected to become critical at a temperature of around 900 K. Therefore, the present simulations predict that an impact velocity of 400 m/s is sufficient to cause ignition in this geometry. By contrast, the temperature increase in the central crack ($\alpha = 45^{\circ}$) is lower than at the HMX-Sylgard interface. At the end of the simulations, $\Delta T = 0.2$ K for $U_p = 10$ m/s, $\Delta T = 41$ K for $U_p = 100$ m/s, and $\Delta T = 27$ K for $U_p = 400$ m/s. These temperatures appear to be insufficient for ignition.



Figure 2.13. Maximum temperature over time in the HMX crystal at different impact velocities U_p . Dashed lines correspond to the cases with initial damage at the HMX-Sylgard interface.

2.3.3 Conclusions

The ability to determine the crack nucleation and propagation during dynamic compression is fundamental to simulating PBX's ignition. The effect of preexisting cracks, impact velocity, and surface defects on HMX-Sylgard systems are studied with 2D simulations in the present work. The PFDM simulations show the effect of initial defects on the damage propagation. Regions with initial debonding between HMX particles and the polymer are critical sites where cracks nucleate and propagate. 3D simulations show that thickness variations of the HMX particles are also crack nucleation sites. This suggests that the cracks observed in the gas-gun experiments in reference [6] can be correlated with surface defects, initial cracks, and interfacial debonding. The comparison with gas-gun experiments allows to estimate the value of the energy release rate, but more experiments and simulations are needed for further calibration.

In particular, a controlled microstructure, with designed cracks and voids in the samples, would represent an ideal system to study defects' dynamics. Experiments with engineered interfaces and microstructures are essential to determine the critical parameters needed to predict temperature fields, such as the friction coefficient and the energy release rate. Simulations of the temperature field induced by friction indicate that this mechanism may be sufficient for ignition at an impact velocity of 400 m/s while an impact velocity of 100 m/s will not. The highest temperature increase is always located where particle cracks intersect the HMX-Sylgard interface. This indicates that debonded interfaces and cracks crossing the particle surface can be critical for forming hot-spots. Other heat sources, such as plastic power, viscous heating, and crack propagation, are not considered in this work and will be studied in future investigations.

Since 1980, friction has been suggested as a possible hot-spot mechanism for energetic materials [105], [106]. However, quantitative predictions remain elusive due to the uncertainty in the friction coefficients and the experiments' complexity and simulations. Dienes [106] developed a theoretical analysis to estimate the heat produced by different heat sources, including the interfacial sliding of a closed crack. Later, the SCRAM model [30], in which a distribution of cracks is considered, was used to simulate impact tests and to estimate the ignition probability of energetic materials. However, SCRAM does not resolve single cracks propagating and interacting. Moreover, SCRAM model does not take into account the particle-binder interface. A mesoscale model as the one presented here that resolves individual particles, interfaces and cracks is needed to predict local temperature increase that may lead to the formation of hot-spots. In particular, particle-binder interfaces, which seem to be critical for the nucleation of hot spots, need to be included.

In summary, the simulations presented here show that different processes and regimes at different strain rates can be identified. At low impact velocity, 10 m/s, cracks propagate predominantly along the direction of the shock wave due to the transversal tensile stress, see Figures 2.8 and 2.10 (a). Crack patterns are strongly dominated by initial defects such as preexisting cracks and interface debonding. Stress waves reflections at interfaces that produce tensile stress are responsible for particle-matrix debonding. At impact velocities of 100 m/s and 400 m/s, debonding of the particle binder interfaces parallel to the stress wave is observed, see Figures 2.10 (b) and (c). Hot spots are nucleated predominately at cracks that intersect the particle/binder interfaces, see Figure 2.12. A local temperature increase of 900 K is observed at an impact velocity of 400 m/s, while a rise of 100 K is obtained for impact velocity 100 m/s, see Figure 2.13.

2.4 Effect of initial damage on hot-spot nucleation in HMX

2.4.1 Numerical model

To study the effect of initial damage and impact velocity on the temperature and damage fields, a particle of β -HMX embedded in Sylgard binder is impacted with velocity U_p on its left boundary similar as in Figure 2.9. Due to symmetry with respect to the *y*-axis, just half of the domain is modeled. The symmetric boundary condition is applied on the bottom boundary (zero vertical velocity), and horizontal displacement is fixed to zero on the right boundary (zero velocity). The top boundary is traction-free (zero normal force). Material properties and phase-field parameters used for all simulations are reported in Table 2.2. The domain is discretized using 58,254-second-order quadrilateral elements with a size of 2.5 μ m. The length scale parameter is set as $l_0 = 10.0 \ \mu$ m. The value $\eta = 0.1 \ \text{s/m}$ has been used previously to simulate β -HMX particles embedded in Sylgard during gas gun experiments at an impact velocity of 400 m/s, at which the damage model becomes rate dependent, and it is suitable to reproduce the characteristic time to damage completely one particle. Initial cracks are introduced using Equation 2.36.

$$c(d) = c_{max} e^{(-|d|/l_0)}$$
, (2.36)

The length, orientation, and c_{max} are chosen randomly from a uniform distribution. Four cases with different initial crack densities ρ_0 and mean length l_c are studied. Representative distributions of each case are shown in Figure 2.14. The initial crack density is calculated as the ratio between the area of the initial cracks and the particle area. The mean crack length l_c is drawn randomly from a uniform distribution span of 20 μ m. Zero heat flux is imposed at the boundary, and the initial temperature is 293 K. Heat generation due to friction and damage propagation are considered. The intensity of both heat sources is determined by the friction coefficient and the fracture energy, respectively. A friction coefficient $\mu = 1.0$ for β -HMX single crystals are used. The temperature increase due to thermoelasticity during shock load is not included because it is smaller compared to the localized heating from friction [74].

2.4.2 Hot-spot detection

The criticality of a hot-spot depends on its size and temperature. For instance, based on Tarver's criterion for ignition [19], shock-induced hot-spots in β -HMX should have temperatures close to 1000 K and size around 1.0 μ m. Therefore, we used a "hierarchical clustering" algorithm to calculate the size and temperature of hot-spots obtained in our simulations. The clustering algorithm works as follows: at a selected time t, the nodes with temperature above a threshold value T_{thres} are identified. A hot-spot is defined as the group of nodes or cluster such that the temperature at every node is above T_{thres} . Given a node n_1 in the group, another node n_2 belongs to the same cluster if their distance is below a threshold r_{max} . In this paper, $T_{thres} = 300$ K for $U_p = 100$ m/s, $T_{thres} = 600$ K for $U_p = 400$ m/s, and $r_{max} = 18.75 \ \mu$ m for both impact velocities, which is three times the average element size. Once a cluster is identified, its temperature is calculated as the weighted average of each cluster's nodal temperatures. The weights are the average size of the elements containing



Figure 2.14. Initial crack distributions in the particle. (a) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 1.7 \ \%$, (b) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 3.4 \ \%$, (c) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 6.9 \ \%$, and (d) $l_c = 100 \ \mu\text{m}$ and $\rho_0 = 6.9 \ \%$.

each node. Finally, the hot-spot size is calculated as the circle's diameter with the same area as the cluster.

2.4.3 Results

Effects of the initial crack distribution

The effects of initial crack density and mean crack length are discussed in this section for impact velocity $U_p = 100$ m/s. Initial damage configurations with two mean crack lengths $(l_c = 50 \ \mu\text{m} \text{ and } l_c = 100 \ \mu\text{m})$, and three initial crack densities ($\rho_0 = 1.7\%$, 3.4%, and 6.9%) are modeled (see Figure 2.14. Three realizations per each initial damage configuration are simulated. The evolution of the damage field for one realization of each damage configuration case is shown in Figure 2.15. It can be observed that the crack pattern is strongly dependent on the initial damage distribution. For $\rho_0 = 1.7\%$, damage nucleates at the left binder/particle interface and advances in the direction of the impacting wave. For larger crack densities, cracks grow and merge inside the particle. Additionally, initial cracks closely oriented along the direction of the impact velocity propagate more readily. These features agree with the fracture patterns observed in gas gun experiments [6], [100]. For the same initial crack density $\rho_0 = 6.9\%$, the case with $l_c = 50 \ \mu m$ shows more crack coalescence. This case has a higher number of initial cracks, approximately twice, compared to $l_c = 100 \ \mu m$.

An estimation of the crack tip velocity can be given from Figure 2.15 as the particle length, 500 μ m, divided by the characteristic time for the cracks to propagate horizontally through the whole particle, 0.8 μ s. This estimated crack tip velocity, 500 μ m / 0.8 μ s = 625 m/s, is around one fourth of the Rayleigh speed, 2.67 km/s. In this regime, inertial resistance to crack propagation is present [99].

The temperature fields for all the cases are shown in Figure 2.16 at time t=0.8 μ s. The highest temperature increase occurs at the left binder/particle interface where temperature values up to 493 K are observed for the case with $\rho_0 = 3.4$ % and $l_c = 50 \ \mu$ m. For $\rho_0 = 1.7$ %, only a region of high temperature is observed at the left binder/particle interface. As the initial density of cracks increases, several hot-spots are seen along with the particle/binder interface and inside the particle, where heat is generated due to friction between crack surfaces. The temperature rises in initial cracks in the particle's interior, but this temperature increase is smaller than the one observed at initial cracks at the particle/binder interfaces.

Figures 2.17 (a) and (b) show the temperature evolution due to frictional heating in the node where the maximum temperature is reached at the end of the simulation. Figures 2.17 (c) and (d) show the maximum temperature increase due to crack propagation only. The location of the node with the maximum temperature increase for these mechanisms is different. In Figures 2.17 (a) and (b) the node with the maximum temperature is always located at cracks intersecting the binder/particle interface while for Figures 2.17 (c) and (d) it occurs inside the particle, but no specific location is identified.



Figure 2.15. Damage phase field evolution of β -HMX particle embedded in Sylgard for the four cases of initial crack distributions (a) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 1.7 \ \%$, (b) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 3.4 \ \%$, (c) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 6.9 \ \%$, and (d) $l_c = 100 \ \mu\text{m}$ and $\rho_0 = 6.9 \ \%$. The binder/particle interface is marked with white contour lines. Regions with phase field value c > 0.95 are white.

In Figure 2.17, different curves with the same color correspond to different realizations with the same initial crack density and average crack length. While the maximum temperature increase due to friction is above 50 K in all the cases, the temperature increase due to crack propagation is always below 40 K after 1 μ s. In general, smaller ΔT_{max} due to friction is predicted for the smallest initial crack density. However, simulations with $\rho_0 = 3.4\%$ and $l_c = 50 \ \mu$ m, see red lines in Figure 2.17(a), show the highest temperature increase. This case corresponds to the initial configuration (b) in Figure 2.14, in which an approximately horizontal initial crack intersects the left binder/particle interface. As soon as the impact



Figure 2.16. Temperature field at $t = 0.8 \ \mu s$ for the four cases with different initial crack distributions impacted at $U_p = 100 \text{ m/s}$, (a) $l_c = 50 \ \mu m$ and $\rho_0 = 1.7 \ \%$, (b) $l_c = 50 \ \mu m$ and $\rho_0 = 3.4 \ \%$, (c) $l_c = 50 \ \mu m$ and $\rho_0 = 6.9 \ \%$, and (d) $l_c = 100 \ \mu m$ and $\rho_0 = 6.9 \ \%$.

wave reaches this interface, the temperature increases suddenly due to frictional heating. The crack length does not appear to have a strong effect on the maximum temperature increase. It is interesting to observe the temperature evolution for the curve that attains the maximum change in temperature in Figure 2.17(d). It can be observed that ΔT_{max} decreases after 0.7 μ s due to heat conduction.

Figure 2.18 shows the hot-spots at $t = 0.5 \ \mu$ s and $t = 1.0 \ \mu$ s calculated using the hierarchical clustering algorithm explained in Section 2.4.2. The size and temperature of the hot-spots increase with time. For the case shown in Figure 2.18(a), at $t = 0.5 \ \mu$ s the temperature increase is almost negligible and no hot-spots are observed. Nevertheless, for initial configurations shown in Figures 2.18(b), (c) and (d) hot-spots with a temperature increase up to 30 K at $t = 0.5 \ \mu$ s are observed. At $t = 1.0 \ \mu$ s fewer hot spots are formed for the



Figure 2.17. Maximum temperature increase in β -HMX particle due to frictional heating for (a) different crack densities ρ_0 and (b) different average crack lengths l_c , and due to damage propagation for (c) different crack densities ρ_0 and (d) different average crack lengths l_c . Different curves with the same color correspond to different realizations with the same crack density and average crack length.

case with the lowest crack density than other cases. In general, hot spots with temperature increase between 40 and 100 K are formed. Again, the initial crack length has no strong effects on the formation of hot spots.

Effects of the impact velocity

The effect of the impact velocity is studied in this section by simulating the same geometries' response to an impact velocity of $U_p=400$ m/s. For the same damage configurations shown in Figure 2.14, three realizations were simulated. Figure 2.19 shows the temperature field at $t = 0.28 \ \mu$ s. Hot-spots are visible in the left-top corner of the particle for all cases. These regions correspond to zones of shear damage localization as observed in [90]. Further-



Figure 2.18. Hot-spots temperature and size at times $t = 0.5 \ \mu\text{s}$ and $t = 1.0 \ \mu\text{s}$, (a) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 1.7 \ \%$, (b) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 3.4 \ \%$, (c) $l_c = 50 \ \mu\text{m}$ and $\rho_0 = 6.9 \ \%$, and (d) $l_c = 100 \ \mu\text{m}$ and $\rho_0 = 6.9 \ \%$. For all cases the impact velocity is $U_p = 100 \ \text{m/s}$.

more, the size and number of the hot-spots increase with the initial crack density. The size and temperature of the hot-spots for impact velocities $U_p = 400$ m/s at time $t = 0.28 \ \mu$ s are shown in Figure 2.20. The hot-spots are compared to Tarver's criterion [19], which states that hot-spots located above the dashed line will cause ignition. Clearly, for $U_p = 100$ m/s, the temperature rise is not high enough to start the ignition of the explosive crystal. When the particle is impacted at $U_p = 400$ m/s, hot-spots with temperature between 600 K and 1500 K are identified at $t = 0.28 \ \mu$ s. As it can be observed in Figure 2.20, several hot-spots are above Tarver's curve of criticality, indicating a high probability of ignition. The majority of these hot-spots belong to cases $\rho_0 = 3.4\%$ with $l_c = 50 \ \mu$ m, and $\rho_0 = 6.9\%$ with $l_c = 100 \ \mu$ m.

2.4.4 Conclusions

A phase-field damage model that couples fracture and heat transfer was developed to study the effect of variability in the initial damage distributions and impact velocity on the



Figure 2.19. Temperature field at $t = 0.28 \ \mu s$ for the four cases with different initial crack distributions impacted at $U_p = 400 \text{ m/s}$. (a) $l_c = 50 \ \mu m$ and $\rho_0 = 1.7 \ \%$, (b) $l_c = 50 \ \mu m$ and $\rho_0 = 3.4 \ \%$, (c) $l_c = 50 \ \mu m$ and $\rho_0 = 6.9 \ \%$, and (d) $l_c = 100 \ \mu m$ and $\rho_0 = 6.9 \ \%$.



Figure 2.20. Hot-spots temperature and size for impact velocity $U_p = 400$ m/s at $t = 0.28 \ \mu$ s.

sensitivity of a β -HMX particle embedded in a Sylgard matrix. This type of geometry with discrete particles has been extensively studied experimentally to distinguish and isolate possible ignition mechanisms that are related only to the particle microstructure [6], [100]. The equations to describe the heat generation by crack propagation and crack surface friction are derived from a thermodynamically consistent model in which crack surfaces and heat sources can be expressed as a function of the damage phase field. The coupled fracture and heat transfer problems are verified on a square domain under different loading conditions. The simulations show that at impact velocity $U_p=100$ m/s and $U_p=400$ m/s, heating due to friction is more important than heating due to dissipation during crack propagation.

The effect of initial damage content and impact velocity on the formation of hot-spots is studied. At impact velocity $U_p = 100$ m/s, there is a large variability in the maximum temperature developed in the particle at time t=1 μ s, see Figure 2.17, even for the same initial crack density and length. At earlier times (0.5 μ s), the lower density of initial cracks is correlated with fewer hot-spots. However, no substantial effects of the initial crack distribution on hot-spots after 1 μ s are observed for the initial crack densities tested.

For an impact velocity $U_p = 400$ m/s, the variability of the hot-spot size and temperature predicted due to different initial crack distributions is more prominent. The primary source of variability is the presence of pre-existing cracks at the particle/binder interface. This can explain the variation of up to 50% in shock sensitivity observed experimentally by Czerski et al. [102] between different batches of high explosives manufactured with the same method. The authors attributed the difference in shock sensitivity to the surface roughness, constituted by dimples with size 10-30 μ m. This surface roughness may indicate microcracks intersecting the particle/binder interface or may constitute nucleation sites for crack propagation.

The present simulations show that the temperature increase is higher at the particle/binder interface, especially in the presence of initial cracks intersecting the interface. This is consistent with the finding that samples with a larger specific interface area, i.e. when the particle size is smaller, show more considerable uncertainty on the ignition probability [107]. With larger interface area densities, it is more probable for an initial crack to intersect the interface. A systematic numerical study of the effect of the particle shape and
angularity, as called by Czerski et al. [102] is necessary to determine the relative importance of the geometry and size of the particles, and the initial crack density.

Following Tarver's criterion, the samples impacted at $U_p = 100$ m/s do not show conditions for ignition while 76% of samples impacted at $U_p = 400$ m/s have hot-spots that lie above the threshold size and temperature curve (see Figure 2.20) after 0.28 μ s. This is in agreement with the experiments of Kerschen et al. [6] that show ignition for an impact velocity of 445 m/s in β -HMX-based PBX with single particles, while no reaction takes place for an impact velocity of 386 m/s. Evidence of chemical reactions in a β -HMX-based PBX has been found at an impact velocity of 50 m/s [108]. Since the present simulations are limited to a single particle inside a polymer, the effect of friction between particles is not present. It could be an additional mechanism for temperature increase.

In the present work, the effect of the β -HMX crystal orientation and plasticity on the temperature increase is not included. Hardin and Zhou [73] have shown that using a viscoplastic model, applied to β -HMX particles in Estane, the threshold velocity, corresponding to 50% probability of ignition, is 15 m/s higher than using a hyperelastic model. Therefore, if plasticity is introduced in the present simulations, a slightly lower probability of ignition than the value 76% of samples impacted at $U_p = 400$ m/s is expected. The temperature range of the hot-spots predicted with our model is close to the temperatures calculated due to plastic deformation, void collapse, and interfacial friction [49]. Our results give further evidence that crack surface friction in particles with initial damage is of crucial importance in agreement with the theory proposed by Dienes et al. [30].

2.5 Simulations of HMX under harmonic excitation

2.5.1 Numerical model

Finite element simulations are performed to determine the behavior of a single β -HMX particle in a binder under harmonic excitation. The material properties used are shown in

Table 2.1. Detailed dimensions and boundary conditions are presented in Figure 2.21. The mesh contains 13,400 first-order quadrangular elements, with size $h = 6.25 \ \mu m$ inside the particle. The mesh is coarser at the Sylgard block's edges, where the element size is 25 μm . Taking advantage of the symmetry, only half the sample is modeled, with symmetric boundary conditions applied to the right side of the mesh, along with plane strain conditions. The top and left sides are traction-free, while the bottom is fixed in the x-direction, and a sinusoidal displacement defined by $u_y = Asin(2\pi ft)$ is applied in the y-direction. Amplitudes $A=2 \ \mu m$ and $4 \ \mu m$, and frequencies $f=190 \ \text{kHz}$ and 210 kHz following Mares et. al experiments [67] are used in the simulations. The excitation amplitudes are larger than the experimental amplitudes to accelerate the damage process. For the temperature model, adiabatic boundary conditions are applied at all the boundaries of the domain. The initial temperature is set to $T_0=293$ K. The phase-field length parameter is $l_0=5h=31.25 \ \mu m$, where h is the element size inside the particle. This choice ensures that the transition from c = 0.0 to c = 1.0 in a crack occurs over several elements. The kinetic coefficient is $\eta =0.1 \ \text{s/m}$, as in previous simulations of impact loading [90].

While experiments show that β -HMX behaves as a brittle material [17], [108], atomistic simulations at high strain rates and large confining pressures show dislocation activity [109]. The surface energy of β -HMX crystals is measured to be around 0.06 J/m² from indentation experiments [17]. To include the effects of plasticity and higher strain rates, the surface energy needs to be increased. Thus, a value of $G_c = 2.0 \text{ J/m}^2$ is used here for HMX following the results of [90], [94]. A value of surface energy similar to other polymers [110], $g_c = 400$ J/m², is used here for Sylgard. This value renders no damage to the polymer, in agreement with experiments [67]. To account for the degradation of the thermal conductivity with damage, k is expressed as a function of the damage phase field as follows:

$$k(c) = (1 - c^2)k^s + c^2k^c , \qquad (2.37)$$



Figure 2.21. Geometry and boundary conditions of the β -HMX particle embedded in Sylgard under harmonic excitation.

where k^s is the thermal conductivity of the solid and k^c of the damaged material. In this work $k^c = 0$ to avoid heat conduction across open cracks.

2.5.2 Results

Figure 2.22 shows the evolution of the damage field for the geometry and boundary conditions in Figure 2.21 with an excitation amplitude $A=4.0 \ \mu\text{m}$ and frequency f=210 kHz. Black regions correspond to a damage field c > 0. Contour plots of the volumetric stress, $\sigma_{vol} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, are also included to visualize the dynamic evolution of the stress wave. The front of the compressive stress wave can be observed between 1 μ s and 2 μ s and a reflected tensile wave after 3 μ s. The stress field becomes complex due to wave reflections at the free boundaries and the particle/binder interface. After 6 excitation cycles (~ t=30.0 μ s) damage starts and propagates along the particle/binder interface.



Figure 2.22. Volumetric stress and damage field at different times for excitation amplitude $A=4.0 \ \mu m$ and frequency f=210 kHz. In the black regions the damage field is c > 0.8.

In Figure 2.23, the stress component σ_{yy} averaged over the particle is plotted as a function of time for excitation frequencies f = 190 and 210 kHz, and amplitudes $A = 2 \ \mu \text{m}$ and $4 \ \mu \text{m}$. For all cases, the magnitude of the stress increases with time until the onset of damage in the particle causes a stress drop. The time to initiate damage increases from 30 μ s to 55 μ s when the amplitude is reduced from 4 μ m to 2 μ m. Furthermore, decreasing the frequency from 210 kHz to 190 kHz leads to reducing the average stress σ_{yy} with time and to a later damage initiation time.

Effect of initial damage

The effect of initial defects, such as cracks in the particle and debonding, is studied in this section. The four different spatial configurations of initial cracks shown in Figure 2.24 at t=2 μ s are used in the simulations. Case A contains a horizontal crack intersecting the



Figure 2.23. Average stress σ_{yy} in the particle as a function of time.

particle/binder interface. In Case B, a vertical crack intersects the bottom of the particle. Cases C and D have damage along with the horizontal and vertical particle/binder interface, respectively. The length of the initial cracks is 125.0 μ m for all cases. The initial cracks are represented using an exponential function that corresponds to the 1D solution of the phase-field equation, given by:

$$c(r) = c_{max} e^{(-|r|/l_0)}$$
, (2.38)

where r is the distance perpendicular to the crack and $c_{max} = 1$. Figure 2.24 shows the evolution of the damage phase field and the volumetric stress in a region around the HMX particle. The applied excitation frequency is f = 210 kHz in the four cases, and the amplitude is $A=4.0 \ \mu\text{m}$. Regions in black correspond to a value of damage phase field c > 0.8. For Cases A and B, the crack grows towards the particle's interior and along the particle/binder interface intersecting the initial crack. In Case B, the crack inside the particle deflects towards the vertical particle/binder interface. Stress concentrations at the crack tip are observed within the particle as well as along the interface. In cases C and D, the crack remains along with the particle/binder interface.



Figure 2.24. Damage evolution in a β -HMX particle with four configurations of initial damage subjected to harmonic excitation with f = 210 kHz and A= 4.0 μ m. Only the region around the β -HMX particle is shown in the figure. In the black regions the damage field is c > 0.8.

The temperature field is shown in Figure 2.25 at $t = 12.0 \ \mu s$ and 17.0 μs . The bottom of the particle is located at $y = 2 \ mm$ and the top at $y = 2.5 \ mm$. The other interface with the binder is at x=1.2mm. In all cases, higher values of temperature are seen along with the particle/binder interfaces compared to the bulk of the particle, in agreement with observations from Chen et al. [66]. Temperatures of up to 330 K are observed along with the bottom interface for Cases C and D at 17 μs . The increase in temperature due to cracks inside the particle is also observed in Cases A and B.



Figure 2.25. Temperature field in the region close to the particle. The bottom of the particle is located at y=2 mm and the top at y=2.5 mm, the other interface with the binder is at x=1.2mm

The time evolution of the average damage field, c_{mean} , and the average temperature increase, ΔT_{mean} , in the particle for the four cases are shown in Figure 2.26. The most significant ΔT_{mean} is observed in the case of B due to the considerable heating at the initial crack and the particle/binder interface. However, the average temperature difference among all cases is only 1K. From the average damage evolution shown in Figure 2.26 (a) it can be observed that the damage growth rate is similar for all cases.

The average temperature is not a good indicator of the sensitivity of the material [19] as the criticality of a hot-spot depends on its size and temperature. Therefore, the size and temperature of the hot-spots are quantified using a single-linkage clustering algorithm. At time t, the nodes with temperature above a threshold value T_{thres} are identified. A hot-spot is defined as the group of nodes or cluster in which the temperature is above T_{thres} and the distance between the nodes belonging to the same cluster is less than r_{max} . In this study, $T_{thres} = 300$ K and $r_{max} = 18.75 \ \mu$ m are used. The size of a hot-spot is the diameter, d_c , of a circle with the same area as the cluster. The temperature of a hot-spot is computed as the area-weighted average of the nodal temperatures in each cluster.



Figure 2.26. (a) Average damage phase field c over time and (b) mean temperature increase ΔT_{mean} in the particle for the four cases with initial damage.

Figure 2.27 shows the hot-spots identified for all the cases at times 10 μ s, 12 μ s, and 17 μ s. As time advances, the hot-spots grow in size, and several new ones are formed. The largest hot-spot is observed in Case D, located at the bottom particle/binder interface with a size of 80 μ m, and a temperature of 327 K. None of the hot-spots detected can be classified as critical based on Tarver's ignition threshold criterion [19]. This criterion states that to be critical, a hot-spot of size $d_c = 40 \ \mu$ m must have a temperature between 800K and 900 K for β -HMX. However, friction over longer periods could lead to temperatures high enough to initiate chemical decomposition, as observed in experiments [67].

Effect of debonded interfaces

The ultrasonic excitation experiments performed by You et al. [61] report a temperature rise of up to 600 K after 50 ms in coated sucrose crystals. In contrast, the temperature in similar crystals with pristine surface did not change significantly. To study this phenomenon, an interface with thickness $t_{int} = 25 \ \mu m$ is added around the particle for the geometry labeled Case A in Figure 2.24. This interface has the same mechanical and thermal properties as the Sylgard binder but with a critical energy release rate of $g_c = 1 \ J/m^2$ to simulate the weak



Figure 2.27. Plots of temperature vs size d_c of hot-spots generated due to frictional heating for (a) case A , (b) case B , (c) case C , and (d) case D.

adhesion between the particle and the polymer due to the coating. Figure 2.28 shows the damage evolution for the coated particle under an excitation with amplitude $A=4.0 \ \mu m$ and a frequency f=210 kHz. Damage nucleates at the bottom interface and propagates along with the interface that intersects the initial crack until the whole particle is debonded from the matrix. In contrast, when the particle is perfectly attached to the binder, cracking inside the particle occurs before debonding, see Case A in Figure 2.24.

The mean temperature increase in the particle over time is compared Case A with a perfectly bonded interface in Figure 2.29. The simulations predict an increase in temperature of 3.0 K after 20 μ s for the coated particle and 0.75 K for the pristine particle. The temperature field evolution for the coated particle is reported in Figure 2.30, the region of

maximum temperature is located at the bottom interface as in the previous cases. This result agrees with experiments that suggest that particle/binder interfaces [61], [67] are preferential sites for the nucleation of hot-spots. The heat rates calculated for all cases are summarized in Table 2.3. The rates are calculated as the average temperature increase in the particle ΔT_{mean} over a time span of 15 μ s. The heat rate is significantly higher when the particle is coated.



Figure 2.28. Damage phase field evolution for a coated particle of β -HMX with an initial horizontal crack, Case A. Only the region around the particle is shown. In the black regions the damage field is c > 0.8.



Figure 2.29. Comparison of the mean temperature increase vs. time for pristine and coated particles.



Figure 2.30. Temperature field at t = 12 and 17 μ s for the coated particle.

Table 2.3. Temperature rates for crystals containing pre-existing defects, subjected to harmonic excitation at $A = 4.0 \ \mu \text{m}$ and f = 210 kHz.

Case	Temperature rate (10^3K/s)
А	13
В	36
С	36
D	30
A (coate	d) 109

2.5.3 Discussion and concluding remarks

Numerical simulations that couple dynamic fracture and heat transport for a single particle in a polymer under periodic dynamic excitation are presented. Heat generation due to friction is incorporated as a heat flux term proportional to the traction and the relative sliding velocities of the crack surfaces. The periodic excitation frequencies are chosen in the range used in ultrasonic excitation experiments [67], [68], and larger amplitudes are assigned to accelerate the damage process to micro-seconds. Simulations of a pristine particle under dynamic excitation show that damage starts at the particle/binder interface. The preferential locations are where the stress wave first impacts the particle or in the vicinity of defects. As expected, higher frequencies and larger amplitudes lead to an increase in the damage growth rate. Initial defects in the particle and cracks at the interface are added to quantify their effect. Adding these defects reduces the time for damage growth and consequently augments heat generation due to friction. Initial cracks in the particle (cases A and B) propagate toward the interior of the particle and accelerate debonding along with the interface they intersect. Even with different distributions of initial defects, the most significant increase in temperature always occurs at the bottom particle/binder interface. The hot-spot with the maximum temperature is found in case D, in which an initial crack is located at the bottom particle/binder interface. Furthermore, heating localization at particle/binder interface agrees with thermographs obtained by Chen et al. [66]. Temperature rates between $13 \cdot 10^3$ K/s and $36 \cdot 10^3$ K/s are obtained when damage at the interface or pre-existing cracks in the β -HMX crystal are considered.

The experiments of You et al. [61] study the effect of debonded interfaces by adding a coat of Teflon to the particles. Temperature rates of up to $20 \cdot 10^3$ K/s were reported in samples with coated sucrose inclusions and 6 K/s in pristine samples. Recent experiments by Roberts et al. [68] studied systems with several particles and showed a more significant increase in temperature when the particles were initially debonded. To study this phenomenon, a weak interface is added by decreasing the value of the surface energy in a layer around the particle. Under these conditions, the temperature rate is increased by 3 $(109 \cdot 10^3)$ K/s). This result gives further evidence to support the experiments that report that heating occurs due to friction between the particle and the polymer [61], [66]-[68]. It is important to emphasize that the experimental heat rates are much lower than those obtained in our simulations. This may result from the discrepancy of excitation amplitudes and frequencies and the high friction coefficient used in our simulations ($\mu = 1$). Assuming that the temperature continues to increase following the same trend seen in our numerical results, the temperature after 2 ms would be 511 K in the coated particle and 319 K for the pristine particle. The experiments by You et al. [61] estimate a temperature after 50 ms of 600 K in the coated particle and 300K in the pristine particle.

In summary, the simulations suggest that the intensity of the thermal localization can be controlled more readily by modifying the bonding properties between the particle and the binder rather than reducing the content of bulk defects in the particle. Due to the sensitivity of the predicted temperatures to the particle/binder surface properties, it is clear that more experimental efforts are needed to characterize these parameters.

3. CHAPTER 3: MODELING SHOCKS IN SINGLE HMX CRYSTALS

Preamble

Sections 3.3 and 3.4 of this chapter have been published in the following papers:

C. A. Duarte, C. Li, B. W. Hamilton. A. Strachan, and M. Koslowski. "Continuum and molecular dynamics simulations of pore collapse in shocked β -tetramethylene tetranitramine (β -HMX) single crystals", Journal of Applied Physics 129, 015904 (2021); https://doi.org/10.1063/5.0025050.

C. A. Duarte, A. Hamed, J. D. Drake, C. J. Sorensen, S. F. Son, W. W. Chen, and M. Koslowski. "Void collapse in shocked β -HMX single crystals: simulations and experiments", Prop., Explos., Pyrotech., (2020), 45, 243; https://doi.org/10.1002/prep.201900251.

3.1 Introduction

HE crystals are highly anisotropic crystals that contain a considerable density of defects such as pores, dislocations, and twin boundaries [12]. The presence of voids, even at the nanometer scale, plays an essential role in the shock initiation of EM [21]. When EMs are dynamically loaded, regions of localized thermal energy known as hot spots are formed due to processes such as void collapse, localized plastic dissipation, shear bands, and friction at cracks [13]. Void collapse is known to result in dominant hot-spots and plays a crucial role in the initiation of chemical reactions, and eventually, a transition to detonation [22], [64]. Hot spots are generated during the collapse of voids due to a variety of processes that depend on void geometry, size, and shock strength. From the dissipation during localized plastic deformation to the expansion and recompression of material and even the formation of ejecta gas molecules under strong shock conditions [24]. Hot-spots with high-enough temperature trigger the chemical decomposition and reaction of the EM, and if the thermal energy in the hot-spot due to exothermic chemistry is generated at a higher rate than the energy dissipated due to heat conduction and endothermic reactions, the hot spot will grow in size and temperature [19]. The growth and agglomeration of these 'critical' hot-spots can lead to a steady-state deflagration, as well as the build-up to a detonation wave [21]-[23]. To achieve scales beyond those of MD and capture the effect of microstructure on hotspot formation, continuum models have been used to explore void collapse. Rai et al. [25] used an Eulerian solver to study the collapse of cylindrical voids in β -HMX. The crystal was modeled using a rate-independent perfectly plastic material where thermal softening was also included. In their simulations, they observed transition from plasticity-dominated to hydrodynamic collapse with jet formation at shock pressures over P= 6.89 GPa. Similarly, Springer et al. [47], used a Johnson and Cook model to capture strain rate, temperature, and total deformation, to simulate shear bands at relatively low shock pressures. However, none of these studies have considered the dependence of plastic deformation on the crystalline orientation. Barton et al. [18], [49], used ALE3D and a dislocation-based crystal plasticity to model the collapse of 10 m diameter void, in a β -HMX single-crystal impacted at $U_p = 1$ km/s. They observed that plastic shear localization led to the formation of melting regions along crystallographic slip planes.

In this chapter, we study the shock response of β -HMX single crystals, a widely used energetic crystal. We assess the accuracy of the continuum model implemented in a FE code by direct comparison with large-scale MD simulations of a crystal containing a single cylindrical void, 80 nm in diameter, shocked normal to the plane (100). The continuum model includes a strain rate-dependent crystal plasticity and heat generation due to plastic dissipation. The elastic constants and slope of the shock vs. particle velocity curve are obtained from MD simulations and used in the continuum model. Other parameters used in the FE simulations, including the artificial viscosity, the fraction of plastic dissipation converted to heat, and the Hugoniot curve parameters, are calibrated by comparing the shock jump response using both techniques. Nano void-collapse simulations are compared between the models with no further calibration, emphasizing the velocity and temperature fields and the void collapse rate obtained in both types of simulations. Simulations of the collapse of a 500 μ m void are also discussed in this chapter. The simulations examine the influence of crystal orientation, impact velocity, and void size on the deformation of a single void in a HMX single crystal. Simulations are compared to the results of a gas gun experiment. The experiment consists of a HMX single crystal sample in which a cylindrical void is introduced by mechanical machining. The void diameter is D=500 μ m, and the impact velocity in the crystal is in the range of 70 to 100 m/s. The experiment is not used to calibrate the model.

3.2 Continuum model

3.2.1 Kinematics

The deformation of a body can be described by the functional $\mathbf{x} = \chi(\mathbf{X}, t)$ which maps a material point \mathbf{X} from the reference configuration $\Omega_0 \subset \mathbb{R}^3$ to a point \mathbf{x} in the current configuration $\Omega \subset \mathbb{R}^3$. When χ is continuously differentiable with respect to \mathbf{X} , the deformation gradient tensor can be obtained from the next expression:

$$\mathbf{F} = \nabla_0 \chi(\mathbf{X}, t) = \partial \mathbf{x} / \partial \mathbf{X} \tag{3.1}$$

where ∇_0 is the material derivative with respect to **X**. The deformation gradient tensor **F** can be further decomposed multiplicatively into thermo-elastic \mathbf{F}_e and plastic \mathbf{F}_p parts as follows:

$$\mathbf{F} = \mathbf{F}_{e}\mathbf{F}_{p}; J = \det(\mathbf{F}_{e}) > 0; \det(\mathbf{F}_{p}) = 1$$
(3.2)

As it can be seen in Figure 3.1, initially, the crystal is deformed plastically from the reference configuration to an intermediate configuration by allowing shear deformation to happen in some of the crystallographic slip systems of the monoclinic β -HMX crystal. Then, the crystal lattice stretches and rotates as prescribed by \mathbf{F}_{e} to reach the current configuration. The velocity gradient is given by:

$$\mathbf{L} = \mathbf{L}_{\mathrm{e}} + \mathbf{F}_{\mathrm{e}} \mathbf{L}_{p} \mathbf{F}_{\mathrm{e}}^{-1} \tag{3.3}$$

where $\mathbf{L}_{e} = \dot{\mathbf{F}}_{e} \mathbf{F}_{e}^{-1}$. The plastic distortion \mathbf{L}_{p} is related to dislocation motion on the slip system s_{i} with plane unit normal $\mathbf{\hat{n}}_{s_{i},0}$ and glide direction $\mathbf{\hat{b}}_{s_{i},0}$, both vectors defined in the reference configuration Ω_{0} [111]:

$$\mathbf{L}_p = \dot{\mathbf{F}}_p \mathbf{F}_p^{-1} = \sum_{i=1}^{N_s} \dot{\gamma}_{pl,s_i} \hat{\mathbf{b}}_{s_i,0} \otimes \hat{\mathbf{n}}_{s_i,0}$$
(3.4)

where N_s is the number of slip systems identified for β -HMX crystals (see Table 3.1) and $\dot{\gamma}_{pl,s_i}$ is the slip rate on each slip system. Following the approach proposed by Luscher et al. [46], [112], the elastic part of the deformation gradient is decomposed multiplicative into isochoric $\hat{\mathbf{F}}_e = J^{-1/3} \mathbf{F}_e$ and volumetric and $\bar{\mathbf{F}}_e = J^{1/3} \mathbf{I}$ parts:

$$\mathbf{F}_{\mathrm{e}} = \hat{\mathbf{F}}_{\mathrm{e}} \bar{\mathbf{F}}_{\mathrm{e}} \tag{3.5}$$

For low symmetry crystals, both volumetric and deviatoric parts of the elastic strain tensor are coupled [46], [112]. Particularly monoclinic crystals such as β -HMX exhibit shearextensional coupling meaning that shear strain may produce normal stress. Then, the elastic Green-Lagrangian strain is additively decomposed in the reference configuration as follows:

$$\mathbf{E}_{\mathrm{e}} = \bar{\mathbf{E}}_{\mathrm{e}} + \hat{\mathbf{E}}_{\mathrm{e}} \tag{3.6}$$

The first term in Equation 3.6 is totally volumetric and defined with respect to the reference configuration as follows:

$$\bar{\mathbf{E}}_{\mathrm{e}} = \frac{1}{2} \left(\bar{\mathbf{F}}_{\mathrm{e}}^{T} \bar{\mathbf{F}}_{\mathrm{e}} - \mathbf{I} \right) = \frac{1}{2} \left(J^{2/3} - 1 \right) \mathbf{I}$$
(3.7)

The second term in Equation 3.6 represents the isochoric part of the deformation. Since $\dot{\mathbf{E}}_{e}$ is defined in an intermediate dilatational configuration, it needs to be pulled back to the reference configuration as follows:

$$\hat{\mathbf{\hat{E}}}_{e} = \bar{\mathbf{F}}_{e}^{T} \hat{\mathbf{E}}_{e} \bar{\mathbf{F}}_{e}$$
(3.8)

Even though the tensor $\hat{\hat{\mathbf{E}}}_{e}$ represents the deviatoric component of the Lagrangian strain tensor, it is also coupled to the volumetric deformation.



Figure 3.1. Kinematics.

3.2.2 Crystal plasticity

The expression used to calculate the shear strain rate $\dot{\gamma}_{pl,s_i}$ shown in Equation 3.9 depends on the type of constitutive crystal plasticity model that is being used. In phenomenological constitutive models, $\dot{\gamma}_{pl,s_i}$ is defined as a function of the resolved shear stress τ_{s_i} and the critical resolved shear stress τ_{th,s_i} . In this work, a power law rule is used to calculate the slip rate as follows [113]:

$$\dot{\gamma}_{pl,s_{i}} = \dot{\gamma}_{0} \operatorname{sign}(\tau_{s_{i}}) \left| \frac{\tau_{s_{i}}}{\tau_{th,s_{i}}} \right|^{1/m}$$
(3.9)

where $\dot{\gamma}_0$ is the reference slip rate, $\tau_{s_i} = 0.5\mathbb{C}[\mathbf{F}_e^T\mathbf{F}_e - \mathbf{I}] : (\mathbf{\hat{b}}_{s_i,0} \otimes \mathbf{\hat{n}}_{s_i,0})$ is the resolved shear stress on the slip system s_i , and m is the rate sensitivity parameter. The slip rate increment in Equation 3.9 is limited by phonon drag $\dot{\gamma}_{pd}$ when dislocation velocity approaches the shear wave speed. The critical resolved shear stress τ_{th,s_i} is obtained using the next expression:

$$\tau_{th,s_i} = r_{s_i} g_{s_i} \tag{3.10}$$

where r_{s_i} is the strength ratio in each slip plane (see Table 3.1), and g_{s_i} is the resistance function which evolves according to the next power law:

$$\dot{g}_{s_{j}} = \sum_{i=1}^{N_{s}} h_{s_{i}s_{j}} \dot{\gamma}_{pl,s_{j}}$$
(3.11)

where $h_{s_i s_j}$ is the hardening matrix [114]:

$$h_{s_i s_j} = q_{s_i s_j} \left[h_0 \left(1 - \frac{g_{s_j}}{g_{sat}} \right)^a \right]$$
(3.12)

The parameters h_0 , g_{sat} , and a are slip system hardening constants whose values were taken from [115] and are shown in Table 3.2. These values are assumed to be the same for all slip systems. The expression $q_{s_is_j}$ is called the latent hardening, which defines the hardening of slip system s_i due to slip activity in other slip systems s_j , and it takes the value of 1.0 for coplanar slips systems s_i and s_j and 1.4 otherwise [116]. The effect of some of the crystal plasticity parameters on the strain-stress curve is shown in Figure 3.2. In this formulation, the flow rule is not explicitly given. In fact any value non zero value of the resolved shear stress τ_{s_i} will cause plastic deformation. However for values of τ_{s_i} less than τ_{th,s_i} the plastic deformation is significantly small. The space configuration of the β -HMX crystal in the $P2_1/c$ space group with respect to the reference coordinate system $\mathbf{x}, \mathbf{y}, \mathbf{x}$ is shown in Figure 3.3. Slip plane normals and slip directions are input in the reference system. This constitutive model is implemented in the software MOOSE [87]. In the crystal plasticity model, stress is updated according to Algorithm 1.



Figure 3.2. Strain vs stress curves showing the effect of (a) load strain rate $\dot{\varepsilon}$, (b) initial slip rate $\dot{\gamma}_0$, (c) slip rate power law exponent m, and (d) hardening exponent a.



Figure 3.3. Space configuration of the β -HMX lattice in the space group $P2_1/c$ with respect to the orthonormal reference system $\mathbf{x}, \mathbf{y}, \mathbf{x}$. The slip plane normal $\hat{\mathbf{b}}_{s_{i},0}$ and slip direction $\hat{\mathbf{n}}_{s_{i},0}$ are defined in the reference system.

Algorithm 1: Incremental update algorithm at each time step n.

1. Given $\mathbf{F}(t) = \mathbf{F}_n$, $\mathbf{F}(t + \Delta t) = \mathbf{F}_{n+1}$, $\mathbf{F}^p(t) = \mathbf{F}_n^p$, initial slip directions $\mathbf{m}_{s_i,0}^{\alpha}$ and normals $\mathbf{n}_{s_i,0}^{\alpha}$, g_{0,s_i} , and initial guess of $\mathbf{S}^*(t) = \mathbf{S}_n^*$, compute:

$$au_{s_{\mathrm{i}}} = \mathbf{S}_{n}^{*} : \left(\mathbf{m}_{s_{\mathrm{i}},0}^{lpha} \otimes \mathbf{n}_{s_{\mathrm{i}},0}^{lpha}
ight)$$

2. Get slip increments in each slip system:

$$\Delta \gamma_{s_{\rm i},p} = \dot{\gamma}_0 \text{sign}(\tau_{s_{\rm i}}) \left| \frac{\tau_{s_{\rm i}}}{\tau_{th,s_{\rm i}}} \right|^{1/m} \Delta t$$

3. Compute new stress \mathbf{S}_{n+1} :

$$\Delta \boldsymbol{\gamma} = \mathbf{I} - \sum_{i=1}^{N} \Delta \gamma_{p,s_i} \left(\mathbf{m}_{s_i,0}^{\alpha} \otimes \mathbf{n}_{s_i,0}^{\alpha} \right)$$
$$\mathbf{F}_{n+1}^{p-1} = \mathbf{F}_n^{p-1} \cdot \Delta \boldsymbol{\gamma}$$
$$\mathbf{F}_{n+1}^{e} = \mathbf{F}_{n+1} \cdot \mathbf{F}_{n+1}^{p-1}$$
$$\tilde{\mathbf{S}}_{n+1}^{*} = \frac{1}{2} \mathbb{C} : \left(\mathbf{F}_{n+1}^{eT} \cdot \mathbf{F}_{n+1}^{e} - \mathbf{I} \right)$$

4. Use Newton-Raphson to calculate correct stress:

$$\mathbb{R} = \mathbf{S}_n^* - \tilde{\mathbf{S}}_{n+1}^*$$
$$\mathbf{J} = \frac{\partial \mathbb{R}}{\partial \mathbf{S}_n^*} = \mathbf{I} - \frac{\partial \tilde{\mathbf{S}}_{n+1}^*}{\partial \mathbf{S}_n^*}$$
$$\mathbf{S}_{n+1}^* = \mathbf{S}_n^* - \mathbf{J}^{-1} \mathbb{R}$$

- 5. Check tolerance:
- If $\left\|\mathbb{R}\right\|_{2}^{2} > TOL$, go to Step 1 and use $\mathbf{S}_{n}^{*} = \mathbf{S}_{n+1}^{*}$.
- Else, accept stress $\mathbf{S}_{n+1} = \mathbf{S}_{n+1}^*$ and go to next time step

Slip system	$\mathbf{\hat{n}}_{s_{\mathrm{i}},0}$	$\mathbf{\hat{b}}_{s_{\mathrm{i}},0}$	$r_{\rm i}$
s_1	(010)	[100]	1
s_2	(011)	[100]	0.963
s_3	$(01\bar{1})$	$[\bar{1}00]$	0.963
s_4	$(\bar{1}02)$	[010]	0.933
s_5	(001)	[100]	1.681
s_6	$(\bar{1}02)$	[201]	0.376
s_7	(011)	$[0\bar{1}1]$	0.931
s_8	$(0\bar{1}1)$	$[0\overline{1}\overline{1}]$	0.931
s_9	$(\bar{1}\bar{1}1)$	$[\overline{1}0\overline{1}]$	0.701
s_{10}	$(1\overline{1}\overline{1})$	[101]	0.701

Table 3.1. Slip systems from literature of β -HMX identified experimentally and in MD simulations, with their respective strength ratio r_i as given in [49].

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Table 3.2. Single crystal plasticity model parameters and material properties used in this work [115].

Parameter	Value	Units
Initial density, ρ_0	1.891	g/cm^3
Specific heat capacity, C_v	2357.3	J/(kgK)
Thermal conductivity, k	0.31	W/(mK)
Reference temperature, T_0	300	Κ
Reference bulk modulus, K_0	17.822	GPa
Gruneisen parameter, Γ	0.7	
Slope hugoniot, s	1.79	
Reference slip rate, $\dot{\gamma}_0$	0.001	ns^{-1}
Slip rate exponent, m	0.1	
Phonon drag slip rate limit	0.0025	ns^{-1}
Hardening matrix, $h_{s_i s_i}$	9.34	MPa
Hardening exponent, a	2.5	
Initial slip resistance g_{s_0}	103.03	MPa
Saturation slip resistance, g_{sat}	155.73	MPa

3.2.3Thermoelasticity theory

In the lagrangian formulation, the balance of linear momentum equation is given by:

$$\nabla_0 \cdot \mathbf{P} + \rho_0 \mathbf{b} = \rho_0 \ddot{\mathbf{u}} \tag{3.13}$$

where \mathbf{P} is the first Piola-Kirchhoff stress, and \mathbf{b} and $\mathbf{\ddot{u}}$ denote the body force and the acceleration per unit mass respectively. The deformation power is given by the next expression:

$$P_d = \int_{\Omega_0} \mathbf{S} : \dot{\mathbf{E}} dV_0 \tag{3.14}$$

where $\mathbf{S} = \mathbf{F}^{-1}\mathbf{P}$ is the second Piola Kirchhoff stress. In a thermoelastic material, the stress depends only on the deformation gradient \mathbf{F} and the internal energy density e. The internal energy e can be obtained as a function of the Helmholtz free energy, temperature Tand entropy η as follows:

$$\mathbf{e} = \Psi + T\eta \tag{3.15}$$

The entropy inequality is given by the next expression:

$$\dot{\eta} + \nabla_0 \cdot (\mathbf{Q}/T) \ge 0 \tag{3.16}$$

For a thermoplastic solid, the Helmholtz free energy $\Psi(\mathbf{E}_{e}, T, \boldsymbol{\xi}_{n})$ is a function of the elastic strain, temperature and the internal variables $\boldsymbol{\xi}_{n}$, where n = 0, ..., N. The internal energy $e(\mathbf{E}_{e}, s, \boldsymbol{\xi}_{n})$ is a function of the elastic strain, entropy density and the internal variables. The internal variables account for effects of microstructural features, such as dislocations or cracks, on the deformation field. Examples of internal variables are the damage phase field, equivalent plastic strain, back stress, and dislocation generation. The rate of the free energy can be obtained applying the chain rule as follows:

$$\dot{\Psi}(\mathbf{E}_{e}, T, \boldsymbol{\xi}_{n}) = \frac{\partial \Psi}{\partial \mathbf{E}_{e}} : \dot{\mathbf{E}}_{e} + \frac{\partial \Psi}{\partial T} \dot{T} + \sum_{n=0}^{N} \frac{\partial \Psi}{\partial \boldsymbol{\xi}_{n}} \dot{\boldsymbol{\xi}}_{n}$$
(3.17)

Using the rate of the internal energy $(\dot{e} = \dot{\Psi} + T\dot{\eta} + \eta\dot{T})$ the entropy inequality can be written as:

$$(\mathbf{S} - \frac{\partial \Psi}{\partial \mathbf{E}_{e}}) : \dot{\mathbf{E}}_{e} + \mathbf{S} : \dot{\mathbf{E}}_{p} - (\eta + \frac{\partial \Psi}{\partial T})\dot{T} - \sum_{n=0}^{N} \frac{\partial \Psi}{\partial \boldsymbol{\xi}_{n}} \dot{\boldsymbol{\xi}}_{n} - (\mathbf{Q} \cdot \nabla_{0}T)/T \ge 0$$
(3.18)

The conjugate forces are defined as $\mathbf{S} = \frac{\partial \Psi}{\partial \mathbf{E}_{e}}$ and $\mathbf{\Xi}_{n} = -\frac{\partial \Psi}{\partial \boldsymbol{\xi}_{n}}$. By definition the entropy is defined as $\eta = -\frac{\partial \Psi}{\partial T}$. Therefore Equation 3.18 can be rewritten as:

$$\mathcal{D} = \mathbf{S} : \dot{\mathbf{E}}_p - \sum_{n=0}^N \frac{\partial \Psi}{\partial \boldsymbol{\xi}_n} \dot{\boldsymbol{\xi}}_n - (\mathbf{Q} \cdot \nabla_0 T)/T \ge 0$$
(3.19)

Equation 3.19 is called the dissipation or Clausius–Duhem inequality. Ignoring high order terms in the thermoelastic part of the free energy, the Helmholtz free energy per unit volume can be written in the following form:

$$\Psi(\mathbf{E}_{\mathrm{e}}, T, \boldsymbol{\xi}_{n}) = \Psi_{0} + \frac{1}{2} \mathbf{E}_{\mathrm{e}} : \mathbb{C} : \mathbf{E}_{\mathrm{e}} - \mathbf{E}_{\mathrm{e}} : \mathbb{C} : \boldsymbol{\alpha} - \frac{\rho_{0} C_{v}}{2T_{0}} (T - T_{0})^{2} - \eta_{0} (T - T_{0}) + \sum_{n=0}^{N} \frac{\partial \Psi}{\partial \boldsymbol{\xi}_{n}} \boldsymbol{\xi}_{n} \quad (3.20)$$

where \mathbb{C}_{ijkl} is the fourth order elasticity tensor, $\boldsymbol{\alpha} = \frac{1}{2} \left[\exp\left(\frac{2}{3}\alpha \left(T - T_0\right)\right) - 1 \right] \mathbf{I} = \frac{1}{3}\alpha_v \mathbf{I}$ is the thermal strain decomposed into deviatoric and volumetric parts respectively, s_0 and Ψ_0 are the stored free energy and entropy at the reference state (temperature T_0 and $\mathbf{E}=0$) due to lattice defects such as dislocations. The decomposition of the lagrangian strain shown in Equation 3.6 makes it possible to split the free energy as follows:

$$\Psi(\mathbf{E}_{\rm e},T) = \Psi_{\rm eos}(J,T) + \Psi_{cpl}(\hat{\hat{\mathbf{E}}}_{\rm e},J,T)$$
(3.21)

The first term in Equation 3.21 represents the volumetric part of the free energy and it is calculated as follows:

$$\Psi_{\rm eos} = \Psi_0 + \frac{1}{2}\bar{\mathbf{E}}_{\rm e} : \mathbb{C} : \bar{\mathbf{E}}_{\rm e} - \bar{\mathbf{E}}_{\rm e} : \mathbb{C} : \alpha_v \mathbf{I} - \frac{\rho_0 C_v}{2T_0} (T - T_0)^2 + \eta_0 (T - T_0)$$
(3.22)

The second term in Equation 3.21 depends on both volumetric and deviatoric parts of the strain and it is obtained substracting Equation 3.22 from Equation 3.20:

$$\Psi_{cpl} = \frac{1}{2} \mathbf{E}_{e} : \mathbb{C} : \mathbf{E}_{e} - \mathbf{E}_{e} : \mathbb{C} : \boldsymbol{\alpha} - \left[\frac{1}{2}K\delta^{2} - K\delta\alpha_{v}\right]$$
(3.23)

By definition, the Second-Piola Kirchoff stress tensor can be obtained from the free energy equation as follows:

$$\mathbf{S} = J_{\mathrm{e}} \mathbf{F}^{-1} \boldsymbol{\sigma} \mathbf{F}^{-T} = \frac{\partial \Psi}{\partial \mathbf{E}_{\mathrm{e}}} = \frac{\partial \Psi_{\mathrm{eos}}}{\partial \mathbf{E}_{\mathrm{e}}} + \frac{\partial \Psi_{cpl}}{\partial \mathbf{E}_{\mathrm{e}}}$$
(3.24)

where σ is the Cauchy stress tensor. The volumetric part of the stress in Equation 3.24 is given by:

$$\frac{\partial \Psi_{\text{eos}}}{\partial \mathbf{E}_{\text{e}}} = -Jp_{\text{eos}}\mathbf{C}_{\text{e}}^{-1} \tag{3.25}$$

where $\mathbf{C}_{e} = \mathbf{F}_{e}^{T} \mathbf{F}_{e}$ is the right Cauchy strain tensor. The pressure p_{eos} is obtained from the Mie-Grüneisen equation of state:

$$p_{eos} = \Gamma \rho_0 C_v \left(T_0 - T \right) \left(\frac{v_0}{v} \right) + \frac{K_0 \chi}{\left(1 - s\chi \right)^2} \left[\frac{\Gamma}{2} \left(\frac{v_0}{v} - 1 \right) - 1 \right]$$
(3.26)

where Γ is the Grüneisen parameter, $\frac{v_0}{v}$ is the specific volume ratio, s is the slope of the hugoniot and $\chi = 1 - \frac{v}{v_0}$. The coupled term of the stress in Equation 3.24 is given by:

$$\frac{\partial \Psi_{cpl}}{\partial \mathbf{E}_{e}} = \mathbb{C} : \left(\mathbf{E}_{e} - \boldsymbol{\alpha}\right) - K_{0} J^{2/3} \left(\delta - \alpha_{v}\right) \mathbf{C}_{e}^{-1} + \frac{\partial \Psi_{cpl}}{\partial P} \frac{\partial P}{\partial \mathbf{E}_{e}}$$
(3.27)

To be able to capture the steep shock discontinuity and provide mesh stabilization, artificial viscosity is included:

$$\mathbf{S}_{vis} = C_0 \rho_0 \frac{\dot{J}_{\rm e} \left| \dot{J}_{\rm e} \right|}{J_{\rm e}^2} h^2 \mathbf{I} + C_1 \rho_0 c_0 \frac{\dot{J}_{\rm e}}{J_{\rm e}} h \mathbf{I}$$
(3.28)

where h is the element size and c_0 is the longitudinal speed of sound. The coefficient C_0 helps to suppress spurious oscillations behind the wave front whereas C_1 spreads the shock front over several elements and lowers the peak amplitude [117], [118]. For shock simulations these coefficients need to be chosen carefully to guaranty that the Rankine-Hugoniot jump conditions are satisfied.

3.2.4 Heat equation

To derive an equation for the temperature rate we start with the first law of thermodynamics which states that the balance of energy is given by the next equation:

$$\frac{D}{Dt}\left(K+U\right) = W + Q_h \tag{3.29}$$

where K is the kinetic energy, U is the internal energy and Q_h is the heat input to the system. These terms can be written individually in the material description as integrals over volume Ω_0 as follows:

$$K = \frac{1}{2} \int_{\Omega_0} \rho_0 \mathbf{v} \cdot \mathbf{v} d\mathbf{X}$$
(3.30a)

$$U = \int_{\Omega_0} \mathbf{e} d\mathbf{X} \tag{3.30b}$$

$$W = \int_{\partial\Omega_0} \mathbf{T} \cdot \mathbf{v} dS + \int_{\Omega_0} \rho_0 \mathbf{f} \cdot \mathbf{v} d\mathbf{X} = \int_{\Omega_0} \left[\frac{1}{2} \rho_0 \left(\mathbf{v} \cdot \mathbf{v} \right) + \mathbf{P}^T : \nabla_0 \mathbf{v} \right] d\mathbf{X}$$
(3.30c)

$$Q_h = -\int_{\partial\Omega_0} \hat{\mathbf{n}} \cdot \mathbf{q}_0 dS + \int_{\Omega_0} \rho_0 r d\mathbf{X} = \int_{\Omega_0} \left[-\nabla_0 \cdot \mathbf{q}_0 + \rho_0 r \right] d\mathbf{X}$$
(3.30d)

where $\mathbf{v} = \frac{D\mathbf{x}}{Dt}$ is the velocity vector, $\mathbf{q}_0 = -k\nabla_0 T$ is the outward heat flux. Plugging these four expression into Equation 3.29 and using the power conjugates $\mathbf{P}^T : \nabla_0 \mathbf{v} = \mathbf{S} : \dot{\mathbf{E}}$ we obtain the local form of the heat equation:

$$\dot{\mathbf{e}} = \mathbf{S} : \dot{\mathbf{E}} - \boldsymbol{\nabla}_0 \cdot \mathbf{q}_0 + \rho_0 r \tag{3.31}$$

The behavior of the material is defined using the next expression of the Helmholtz free energy:

$$\Psi = \hat{\Psi}(\mathbf{E}_{\rm e}, T) \tag{3.32}$$

Differentiating Equation 3.15 with respect to time $(\dot{\Psi} = \dot{e} - \dot{T}\eta - T\dot{\eta})$ and substituting into Equation 3.31:

$$\dot{\Psi} = \mathbf{S} : \dot{\mathbf{E}} - \dot{T}\eta - T\dot{\eta} - \nabla_0 \cdot \mathbf{q}_0 + \rho_0 r \tag{3.33}$$

where $\mathbf{S} = \mathbf{S}_c + \mathbf{S}_{vis}$ is the Second Piola-Kirchhoff stress tensor, which is formed by conservative and dissipative parts, and $\dot{\mathbf{E}} = \dot{\mathbf{E}}_e + \dot{\mathbf{E}}_p$ is the rate of the Lagrangian strain decomposed into elastic and plastic parts. Using the chain rule to differentiate Equation 3.21:

$$\dot{\Psi} = \frac{\partial \hat{\Psi}}{\partial \mathbf{E}_{e}} : \dot{\mathbf{E}}_{e} + \frac{\partial \hat{\Psi}}{\partial T} \dot{T}$$
(3.34)

The state relations as a function of the Helmholtz free energy are:

$$\mathbf{S}_{c} = \frac{\partial \hat{\Psi}}{\partial \mathbf{E}_{e}}, \eta = -\frac{\partial \hat{\Psi}}{\partial T}, C_{v} = T \frac{\partial \eta}{\partial T}$$
(3.35)

Differentiating the entropy with respect to time:

$$\dot{\eta} = \frac{d}{dt} \left(-\frac{\partial \hat{\Psi}}{\partial T} \right) = -\frac{\partial}{\partial T} \left(\dot{\Psi} \right) = -\frac{\partial^2 \hat{\Psi}}{\partial \mathbf{E}_{\mathrm{e}} \partial T} : \dot{\mathbf{E}}_{\mathrm{e}} + \frac{\partial \eta}{\partial T} \dot{T}$$
(3.36)

Substituting Equations 3.34 and 3.35 into Equation 3.33:

$$C_{v}\dot{T} = \beta_{p}\mathbf{S}_{c}: \dot{\mathbf{E}}_{p} + \beta_{v}\mathbf{S}_{vis}: \dot{\mathbf{E}} + T\frac{\partial^{2}\hat{\Psi}}{\partial\mathbf{E}_{e}\partial T}: \dot{\mathbf{E}}_{e} - \boldsymbol{\nabla}_{0}\cdot k\boldsymbol{\nabla}_{0}T + \rho_{0}r$$
(3.37)

In Equation 3.37, the terms in the right hand side of the equation represent heat generation due to plastic flow, shock viscosity, thermo-elasticity, Fourier's law with thermal conductivity k, and any other heat source. The parameter β_p is known as the Taylor-Quinney coefficient and it is included because not all the plastic dissipation is converted into heat, part of the energy is used to transform the microstructure by creating lattice defects [119]. The second term includes the artificial viscosity which reduces numerical oscillations and smears out the shock front. This approach is used to incorporate the dissipative processes [120] in the shock front and recently has been related to the production of entropy in compression [121]. Following the same approach used with the plastic dissipation we incorporate a factor β_v , assuming that only part of this energy is converted into temperature. The third term is the heat generated due to thermoelastic coupling [46], and it is given by the next expression:

$$\rho_0 T \frac{\partial^2 \Psi}{\partial \mathbf{E}_{\mathrm{e}} \partial T} : \dot{\mathbf{E}}_{\mathrm{e}} = \rho_0 T \frac{\partial^2 \Psi_{\mathrm{eos}}}{\partial \mathbf{E}_{\mathrm{e}} \partial T} : \dot{\mathbf{E}}_{\mathrm{e}} + \rho_0 T \frac{\partial^2 \Psi_{cpl}}{\partial \mathbf{E}_{\mathrm{e}} \partial T} : \dot{\mathbf{E}}_{\mathrm{e}}$$
(3.38)

where:

$$\rho_0 T \frac{\partial^2 \Psi_{\text{eos}}}{\partial \mathbf{E}_{\text{e}} \partial T} \dot{\mathbf{E}}_{\text{e}} = -\Gamma \rho_0 C_v T \text{Tr} \left(\mathbf{C}^{-1} : \dot{\mathbf{E}}_{\text{e}} \right)$$
(3.39a)

$$\rho_0 T \frac{\partial^2 \Psi_{cpl}}{\partial \mathbf{E}_{e} \partial T} \dot{\mathbf{E}}_{e} = -\frac{\alpha T}{3} \exp\left(\frac{2}{3}\alpha(T - T_0)\right) \dot{\mathbf{E}}_{e} : \mathbb{C} : \mathbf{I} + K\alpha T J^{2/3} \exp\left(\frac{2}{3}\alpha(T - T_0)\right) \operatorname{Tr}\left(\mathbf{C}^{-1} : \dot{\mathbf{E}}_{e}\right)$$
(3.39b)

3.2.5 Calibration with MD

In this section, we compare finite element (FE) and molecular dynamics (MD) simulations of shock propagation in a defect-free HMX. These simulations are used to calibrate the coefficients C_0 and C_1 in the artificial viscosity and the slope of the Hugoniot equation, s, used in Equations 3.28 and 3.26. The relation between the shock and particle velocities (U_s and U_p) can be approximated as:

$$U_s = sU_p + s_0 \tag{3.40}$$

where s_0 is the sound speed in the shock direction and the slope, s, is associated with the stiffening of the material with compression. The slope of the Hugoniot is needed in the EoS, Equation 3.40, a constitutive equation that relates pressure and volume. The value of s for HMX can be found in literature and ranges from 1.79 to 2.9 for the {010} orientation [122], [123].

The MD simulations were performed using an all-atom interatomic potential developed by Smith and Bharadwaj [124]. All simulations were run using a β -HMX single crystal (space group P21/n) at the density predicted by the potential at ambient conditions. The LAMMPS MD code was used for all simulations [125]. Explicit MD simulations of shockinduced pore collapse in β -HMX single crystals were conducted. The details can be found in a recent paper by Li et al. [126]. Free surfaces are created along the shock direction [010]to form the impact surface and avoid image interactions. Periodic boundary conditions are applied along the transverse directions, i.e., [100] and [001]. We considered cylindrical pores (with symmetry axes along [001]) of 80 nm in diameter. The simulation cell is 251.68 nm x 298.26 nm x 1.517 nm and contains approximately 11.6 million atoms. Shock loading is along [010] with a $(0\overline{1}0)$ impact plane. We simulate the shock by launching the HMX sample with the desired particle velocity into a fixed piston consisting of a very thin HMX slab (\sim 1.0 nm), which results in a supported shock. The particle velocities we considered include 0.5 km/s, 1.0 km/s and 2.0 km/s. We also compared FE results with MD simulations using the Hugoniostat method [127]. In this technique, the shock is modeled without propagating a wave inside the material in a fully periodic system, allowing for extended simulations and long-time averaging of shock properties. Given a desired shock pressure, the constant stress Hugoniostat couples an integral feedback uniaxial barostat and ergostat to drive the system to the shock pressure while conserving the Hugoniot jump conditions described in Chapter 1.

The geometry used in the simulations is shown in Figure 3.4. In the FE simulations we used plain strain conditions and the orientation relative to the β -HMX unit cell is indicated. We discretized the domain using quadrilateral elements with size in the range 2 – 4 nm, for a total of 13,365 elements. We applied boundary velocities $U_p = 0.2, 0.5, 1.0, 1.5$ and 2.0 km/s on the bottom boundary of the domain along the [010] direction as shown in Figure 3.4. We impose periodic boundary conditions in the transverse directions and the top boundary is traction free. The slope of the Hugoniot in Equation 3.40 was obtained from a linear fit of the MD Hugoniotstat $U_s - U_p$ data in Figure 3.5,(c), which consists of independent compression simulations for each Hugoniot point, determined by input shock pressure. This results in s=2.29 and $s_0=3.33$ km/s. The comparison of the jump conditions for pressure

and temperature obtained from both FE and non-reactive MD simulations, for different U_p are shown in Figure 3.5 (a) and (b).



Figure 3.4. Geometry, boundary conditions, and crystal orientation used for the shock simulations in β -HMX perfect crystals.



Figure 3.5. (a) Temperature and (b) pressure jump as a function of piston velocity U_p obtained from FE simulations and MD Hugoniotstat and direct shock simulations (MD piston).

3.3 Studies of nano-void collapse in HMX

3.3.1 Numerical model

Void collapse is a widely used example problem to establish the validity of numerical simulations of shocks in energetic materials [25], [47], [55], [128]. Unfortunately, minimal comparison with experimental results are available. A limited number of publications discuss the differences among different models [55], [56]. In this section, we perform FE and MD simulations of void collapse with varying velocities of impact.

Figure 3.6(a) shows the geometry and crystal orientation used in the 2D plane strain FE simulations of pore collapse. The element size ranges from 2 to 4 nm. The simulation domain consists of a 250 nm x 300 nm slab containing a cylindrical void of diameter d=80 nm, as shown in Figure 3.6 (b). In MD, the void is cut carefully considering the tilting of the monoclinic simulation cell in the thickness direction; note that the MD simulations are carried out with the relaxed simulation cell predicted by the force field where the monoclinic angle deviates by a few degrees from the experimental value, see Section S3 in the Supplementary Material. Initial velocities $U_p = 0.5$, 1.0 and 2.0 km/s are applied to the bottom boundary in the [010] direction. Periodic boundary conditions are applied on the left and right sides of the domain, and the top boundary is fixed in the vertical direction. The material properties and model parameters used in the FE simulations are consigned in Tables 3.3 and 3.4.



Figure 3.6. Geometry and boundary conditions used for (a) FE and (b) MD pore collapse simulations.

Parameter	Value	Units
Initial density, ρ_0	1.85	g/cm^3
Specific heat capacity, C_v	2357.3	J/(kgK)
Thermal conductivity, k	0.31	W/(mK)
Reference temperature, T_0	300	Κ
Reference bulk modulus, K_0	14.24	GPa
Gruneisen parameter, Γ	0.7	
Slope Hugoniot, s	2.29	
Reference bulk sound speed, C_s	2.77	$\rm km/s$
Reference slip rate, $\dot{\gamma}_0$	0.001	ns^{-1}
Slip rate exponent, m	0.1	
Phonon drag slip rate limit	0.0025	ns^{-1}
Hardening matrix, $h_{s_i s_i}$	9.34	MPa
Hardening exponent, a	2.5	
Initial slip resistance g_{s_0}	103.03	MPa
Saturation slip resistance, g_{sat}	155.73	MPa
Artificial viscosity coefficient, C_0	0.1	-
Artificial viscosity coefficient, C_1	1.0	-

Table 3.3. Material properties and model parameters used in the constitutive model for β -HMX crystals [49], [129].

Table 3.4. Elastic moduli of β -HMX in GPa (Voigt notation) [130].

								-		
C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}
25.1	9.7	12.8	0.0	-1.3	0.0	22.3	11.8	0.0	4.6	0.0
C_{33}	C_{34}	C_{35}	C_{36}	C_{44}	C_{45}	C_{46}	C_{55}	C_{56}	C_{66}	
21.8	0.0	14	0.0	97	0.0	3 18	11.036	0.0	8 66	

3.3.2 Results

3.3.2.1 Velocity magnitude

Figures 3.7, 3.8, and 3.9 show 2D fields of the velocity along the shock direction obtained from FE and MD simulations for $U_p = 0.5$ km/s, 1.0 km/s, and 2.0 km/s. The contour plots correspond to various instants before the void entirely collapses. We define a collapse time, t_c , set to be zero when the shock reaches the front edge of the void. Furthermore, the time t_c is normalized by a characteristic value defined as the time it takes the unperturbed shock to traverse the diameter of the void ($\tau = d/U_S$). Importantly, the continuum model captures the transition from viscoplastic pore collapse at $U_p = 0.5$ km/s to a hydrodynamic regime at $U_p = 2$ km/s.

For $U_p = 0.5$ km/s similar velocity magnitudes are obtained with both models, but the velocity field is more diffused in the FE results. MD simulations show velocity magnitudes up to 1.3 km/s in small regions where deformation localizes into narrow bands. These shear bands are formed due to local inhomogeneities in the void surface that induce localization of plasticity and stress concentrations during shock compression. The surface of the void in the continuum model is homogeneous, therefore, the stress and strain fields are smooth, and no deformation localization is predicted. At small scales these shear bands can be resolved with FE simulations [131], however, this increases the computational effort and cannot be resolved at length scales relevant to the microstructure.

For the case of $U_p = 1.0$ km/s, the velocity fields agree up to $t_c/\tau = 0.84$. At later times, the velocity in the MD simulations is greater at the edge of the void (see Figure 3.8 at $t_c/\tau=1.74$). Figure 3.9 shows the velocity field evolution for $U_p = 2.0$ km/s. The FE velocity fields agree with the MD simulations during the early stages of the void collapse, but the velocity of the void surface is lower in the FE simulations when the expanding material is about to impact the upstream surface. The results show the formation of a central jet structure, traveling at a velocity approximately 6.9 km/s in MD while in FE simulations the jet velocity is 4.23 km/s at time $t_c/\tau=1.38$. At this impact velocity both models capture the transition from viscous pore collapse to the hydrodynamic regime.

We attribute the discrepancy in the velocity field at later times to two factors. First, the of plastic strain localization observed at the void edge in the MD simulations affects more the results for $U_p = 0.5$ km/s and 1.0 km/s. At these impact velocities, as the wave passes the void, shear bands form at the lateral edges of the void. The existence of these shear bands makes atoms to move towards the center of the void to relieve shear stress build-up, which accelerates the void collapse process [55]. At $U_p = 2.0$ km/s, the deformation is

dominated by the pressure and therefore, the effects of plasticity are less important. As a result, shear bands are not observed but instead, the material becomes amorphous around the void. These two mechanisms, shear banding and amorphization, are not included in the continuum simulations and therefore, the velocity field around the void has a smaller magnitude.



Figure 3.7. Fields of velocity along shock direction obtained from FE and MD simulations, during the collapse of a void with diameter d= 80 nm in a β -HMX crystal impacted at $U_p = 0.5$ km/s. The contour plots are taken at instants $t_c = 0, 8, 17, \text{ and } 29 \text{ ps} (t_c/\tau = 0, 0.40, 0.85, \text{ and } 1.45).$

3.3.2.2 Temperature field

Figures 3.10, 3.11 and 3.12 compare the MD and FE temperature fields for various shock strengths and times. For $U_p = 0.5$ km/s, Figure 3.10, temperature fields are shown at t_c/τ = 0, 0.40, 0.85, and 1.45. Regions with higher temperature are observed along the sides of the void towards the upstream area after $t_c/\tau = 0.85$ in both models. The MD simulation shows temperature localization into bands starting around after $t_c/\tau = 0.85$. These bands emanate from both sides of the void and initiate as surface roughness around the void edge appears as the material is extruded into the void. The high-temperature bands from due to shear-banding and plasticity induced heating. The high-temperature bands form



Figure 3.8. Comparison of velocity contour plots obtained from FE and MD simulations, during the collapse of a void with diameter d= 80 nm in a β -HMX crystal impacted at $U_p = 1.0$ km/s. The contour plots are taken at instants $t_c = 0, 9, 13, \text{ and } 27 \text{ ps} (t_c/\tau = 0, 0.58, 0.81, \text{ and } 1.74).$

due to plasticity induced heating by shear dominated deformation. In the FE simulations, temperature spikes originate at similar locations generated by plastic flow localization, but the degree of localization is smaller. As the shock wave passes, the void closes, conserving its aspect ratio. This has been observed in other studies of void collapse at similar [55], [128].

Figure 3.11 shows the temperature evolution for $U_p = 1.0$ km/s at $t_c/\tau=0$, 0.58, 0.81, and 1.74. The MD simulation shows regions of localized temperature bands form before the shock reaches the void, and then they are more prominent on the sides of the void extending to the sides of the domain. Again, the FE simulations show temperature rise in similar locations. For $U_p = 2.0$ km/s, temperature contour plots at $t_c/\tau=0$, 0.64, and 1.38 are shown in Figure 3.12. In both MD and FE simulations, there is a central hydrodynamic jet, and temperature increases behind the jet with similar patterns.



Figure 3.9. Comparison of velocity contour plots obtained from FE and MD simulations, during the collapse of a void with diameter d= 80 nm in a β -HMX crystal impacted at $U_p = 2.0$ km/s. The contour plots are taken at instants $t_c = 0, 7, \text{ and } 15 \text{ ps } (t_c/\tau = 0, 0.64, \text{ and } 1.38).$

3.3.2.3 Temperature distribution

The lack of atomistic mechanisms in FE simulations, in contrast with MD simulations, is a necessary compromise to achieve the scales associated with the microstructure. More essential to develop predictive capabilities for HE materials is the overall distribution of temperature fields. Following [126], we calculate the area with temperature exceeding a given threshold value, T, in the temperature field shown in Figures 3.10, 3.11, and 3.12. For the MD data, the temperature used in the distribution plots was obtained by averaging local temperatures using a square grid with an area of $1 nm^2$. The resolution of the FE results is given by the mesh element size.

Figure 3.13 shows the temperature versus the area obtained from MD and FE simulations for shocks at $U_p = 0.5$ km/s, 1.0 km/s, and 2.0 km/s at $t_c=29$, 27 and 15 ps respectively $(t_c/\tau=1.45, 1.74, \text{ and } 1.38)$. As expected, the temperature increases with U_p . We find


Figure 3.10. Comparison of temperature contour plots obtained from FE and MD simulations, during the collapse of a void with diameter d= 80 nm in a β -HMX crystal impacted at $U_p = 0.5$ km/s. The contour plots are taken at instants $t_c = 0, 8, 17, \text{ and } 29 \text{ ps} (t_c/\tau=0, 0.40, 0.85, \text{ and } 1.45).$



Figure 3.11. Comparison of temperature contour plots obtained from FE and MD simulations, during the collapse of a void with diameter d= 80 nm in a β -HMX crystal impacted at $U_p = 1.0$ km/s. The contour plots are taken at instants $t_c = 0, 9, 13$, and 27 ps ($t_c/\tau = 0, 0.58, 0.81$, and 1.74).



Figure 3.12. Comparison of temperature contour plots obtained from FE and molecular dynamics MD simulations, during the collapse of a void with diameter d= 80 nm in a β -HMX crystal impacted at U_p = 2.0 km/s. The contour plots are taken at instants t_c = 0, 7, and 15 ps (t_c/τ =0, 0.64, and 1.38).

good agreement between MD and FE in the temperature distribution for areas larger than $100 \ nm^2$. In these regions, the temperature increases due to the shock wave and plastic deformation. However, higher peak temperatures at the core of the hot-spots are observed in MD simulations compared to FE. The discrepancy is attributed to the higher degree of plastic deformation localization, larger velocities, and amorphization in the MD simulations.

3.3.2.4 Void collapse rate

The rate at which voids collapse during the shock passage is a quantitative measure used to compare simulations and to validate models against experiments [25], [55]. Figure 3.14 (a) shows the time evolution of the void area. The area, A(t), is normalized by the initial void area, A_0 , and the time $\tau = d/U_S$ is the normalized by a characteristic value defined as the time it takes the unperturbed shock to traverse the diameter of the void. As expected, the void collapse rate increases with the impact velocity. Following the work in [55] we define



Figure 3.13. Area with temperature exceeding T during the collapse of a nanovoid with diameter d = 80 nm, at $t_c=29$, 27 and 15 ps ($t_c/\tau=1.45$, 1.74, and 1.38) for $U_p=0.5$, 1.0, and 2.0 km/s respectively. Solid lines represent FE results, and circular markers are MD results.

the normalized void collapse rate, $\langle A \rangle$, as the slope of a linear fit between $A(t)/A_0$ and t/τ :

$$A(t)/A_0 = -\langle A \rangle \frac{t}{\tau} + b \tag{3.41}$$

The slope is obtained when the pore ratio is in the range of 0.2 to 0.9. These results are shown in Figure 3.14 (b) for different impact velocities. The normalized void collapse rate increases with piston velocity U_p as seen in similar studies in HEs [55]. The void collapse rate increases significantly during the transition from viscoplastic pore collapse and the hydrodynamic regimes and saturates for high velocities.

At the initial stages, the rate for MD and FE simulations are similar, see Figure 3.14 (a). However, during the final stages, the rates from the MD simulations are higher for $U_p = 0.5$ km/s and 1.0 km/s. For the two lower impact velocities the deformation of the void is affected by shear stress and therefore, plastic deformation is important. Increasing the

amount of plastic deformation for these two velocities will increase the void collapse rate. For higher impact velocities the shape of the deformed void is dominated by the pressure and the plastic deformation does not affect the void collapse rate. Therefore, For $U_p = 2.0$ km/s the curves in Figure 3.14 (a) remain close. Given that the plastic deformation is limited by the phonon drag limit, we discuss the effect of plasticity by modifying this quantity in the next section.



Figure 3.14. (a) Void area ratio versus time, FE and MD results are shown as solid and dashed lines. (b) Comparison of the normalized void collapse rate for different U_p .

3.3.2.5 Effect of the phonon drag limit

In the continuum model, the slip rate is limited by the phonon drag limit, $\dot{\gamma}_{pd}$. This quantity limits the slip rate taking into account that the maximum shear wave speed bounds the dislocation velocity. The value of $\dot{\gamma}_{pd}$ can be approximated using the time derivative of Orowan's equation, $\dot{\gamma} = N_m bv$, with a Burger's vector b=1.10 nm, the maximum dislocation velocity bounded by $v = c_s = 2.3$ km/s, and assuming a dislocation density N_m . As the dislocation density augments during deformation, the phonon drag limit should also increase. However, in our current model, the phonon drag limit is set to a constant value. To study the effect of the phonon drag limit on the void collapse rate and temperature field, we compare two FE simulations using $\dot{\gamma}_{pd}=2.5 \ ns^{-1}$ and $\dot{\gamma}_{pd}=5.0 \ ns^{-1}$. These values correspond to a maximum mobile dislocation density of $N_m=1.0 \ m^{-12}$ and $N_m=2.0 \ m^{-12}$, respectively. Figure 3.15(a) shows the comparison of the time evolution of the void area ratio and Figure 3.16 compares the temperature distribution. Given that the void collapse rate is dominated by the pressure at $U_p=2.0 \ \text{km/s}$, similar deformation is obtained using $\dot{\gamma}_{pd}=2.5 \ ns^{-1}$ and $\dot{\gamma}_{pd}=5.0 \ ns^{-1}$. For lower impact velocities the effect of shear stresses is more important and therefore, the void collapse rate is reduced when the plastic deformation is restrained by a lower phonon drag limit. Figure 3.15(b) shows the velocity fields obtained with $U_p=0.5 \ \text{km/s}$ and using $\dot{\gamma}_{pd}=2.5 \ ns^{-1}$ and $\dot{\gamma}_{pd}=5.0 \ ns^{-1}$ at time $t_c/\tau=3$. The velocity magnitude is reduced when the phonon drag limit is decreased.

In Figure 3.16 the temperature distributions are compared at different times after the shock wave has passed through the void. For $U_p = 0.5$ km/s, the temperature distribution is similar for both values of $\dot{\gamma}_{pd}$, see Figure 3.16 (a) and (b) due to the limited plastic deformation rate at lower impact velocities. For $U_p = 1.0$ km/s and 2.0 km/s a smaller phonon drag limit restricts plastic strain rate and a larger difference in temperature is observed. Furthermore, the effect is cumulative and more noticeably at later times $(t_c/\tau > 1)$. These results suggest the importance of accurate plasticity models and incorporating realistic values of phonon drag to predict plastic deformation at high impact velocities that will determine temperature field distributions.



Figure 3.15. (a) Effect of the phonon drag limit on the void area ratio in FE simulations. Solid lines are results with $\dot{\gamma}_{pd}=5.0 \ ns^{-1}$ and dashed lines are for $\dot{\gamma}_{pd}=2.5 \ ns^{-1}$.(b) Effect of the phonon drag limit on the velocity magnitude for $U_p=0.5 \text{ km/s}$ and $t_c/\tau=3$.



Figure 3.16. Area with temperature exceeding T during the collapse of a nanovoid with diameter d = 80 nm, at (a) earlier, and (b) later times during the collapse of the void. Solid lines are results with $\dot{\gamma}_{pd}$ =5.0 ns^{-1} and dashed lines are for $\dot{\gamma}_{pd}$ =2.5 ns^{-1} .

3.3.3 Conclusions

We presented FE and MD simulations of the shock response in single β -HMX crystals containing a single nano-size void. The FE model includes anisotropic elastic and inelastic deformation using a rate-dependent crystal plasticity model, and equation of state and heat transport. In the FEM model the only sources of heat are the shock dissipation and plasticity. The anisotropic elastic constants were obtained from MD simulations and non-reactive Hugoniot and direct shock MD simulations in homogeneous β -HMX were used to inform the continuum model by calibrating the slope of the Hugoniot equation and the temperature jump through the values β_v and β_p .

The velocity, temperature and void collapse rate obtained with non-reactive direct shock MD and FE simulations with different particle velocities were compared without further calibration. Both models capture the transition from viscoplastic to hydrodynamic void collapse at impact velocities larger than 1 km/s. The velocity field around the void predicted with FE and MD agreed during the first stages of the void collapse for all impact velocities. After longer times, the upstream surface of the void travels at a higher velocity in the MD simulations. This behavior is also reflected when the void collapse rates are calculated, with a slower rate for the FE simulations specially at lower impact velocities. The better agreement in the void collapse evolution at larger impact velocities occurs because under these conditions the deformation field is dominated by pressure and the equation of state is fully informed from MD simulation. However, local deformation and the jet velocity is influenced by plastic deformation. The lack of localization of plastic deformation in the FE simulations is responsible for the disagreement of the velocity fields. However, other mechanisms not included, such as amorphization and local melting may contribute too.

The temperature increases at similar locations around the void for MD and FE simulations. For impact velocities $U_p = 0.5$ km/s and 1.0 km/s regions of large temperature are localized into shear bands in the MD simulations. In general, the temperature distributions are higher in the MD simulations at later times, $t_c/\tau > 1$. Given that the shock temperature agrees in both models, again the difference may be attributed to the plasticity model and other dissipative mechanisms not included in the FE model.

To understand the effect of plasticity on temperature and void deformation we modified the value of the phonon drag limit. This parameter restricts the amount of plasticity rate allowed in the FE simulations. We found that the phonon drag limit has a strong influence on the void collapse rate and the velocity fields at lower impact velocities. This is due to the importance of shear stresses that drive plasticity during viscoplastic deformation. In contrast, at larger impact velocities the plastic deformation does not affect the void collapse rate because the deformation is dominated by pressure. As expected, a higher value of $\dot{\gamma}_{pd}$ renders more plastic deformation and therefore, the temperature field increases with phonon drag limit. In summary, the phonon drag limit restricts plastic deformation rate, which at lower impact velocities affects the void collapse rate while at higher velocities impacts the maximum temperature.

This work gives further evidence that continuum plasticity models for energetic materials need further investigation. For example, accounting for the dislocation density to calculate the phonon drag limit is of primary importance. Furthermore, other mechanisms that induce strain localization and amorphization should be incorporated in computational continuum models of energetic materials.

3.4 Studies of micro-void collapse in HMX

3.4.1 Numerical model

The void dynamic response is simulated using the 2D geometry shown in Figure 3.17. It consists of a β -HMX single crystal containing a void of diameter D = 10 μ m and D = 500 μ m. Three different crystal orientations are simulated with the x-axis oriented parallel to the (100), (010), and (110) crystal plane normals. All the directions are defined in the $P2_1/c$ space group. The crystal is impacted on its left boundary applying velocities $U_p = 0.1$ km/s, 0.5 km/s, and 1 km/s. Plane strain conditions were used in all simulations. The 2D domain

was discretized using triangular elements. The mesh was refined around the void, giving an element size h in the range 0.39-1.0 μ m for the simulations with void size $D=10 \ \mu$ m, and 19.6-50.0 μ m for $D=500 \ \mu$ m.

Material properties and model parameters used for all simulations are reported in Tables 3.5 and 3.6. The elastic constants were determined from non-reactive molecular dynamics simulations at room temperature by Hamilton, and Strachan [130], using the force field developed by Smith and Bharadwaj [124] in the software LAMMPS [125]. Six representative snapshots of the dynamic evolution of the void are presented in Figure 3.18 with an impact velocity of 0.5 km/s applied to the polymer. Using the impedance of both binder and β -HMX, a gas gun velocity of 0.5 km/s applied on the binder corresponds approximately to a $U_p = 0.1$ km/s at the crystal. Figure 3.18 (a) contains the initial void. The left surface of the void starts moving after 0.4 μ s in Figure 3.18 (b). No jetting is observed, and this regime corresponding to viscoplastic void collapse response.



Figure 3.17. Geometry and boundary conditions used for the void collapse simulations.



Figure 3.18. Snapshots of the evolution of the 500 μ m cylindrical void, (a) initial void, (b)t = 0.4 μ s, (c) t = 0.6 μ s, (d) t = 0.8 μ s, (e) t = 1.2 μ s, and (f) t = 1.6 μ s.

Table 3.5. Material properties and model parameters used in the constitutive model for β -HMX crystals [49], [129].

Parameter	Value	Units
Initial density, ρ_0	1.891	g/cm^3
Specific heat capacity, C_v	2357.3	J/(kgK)
Thermal conductivity, k	0.31	W/(mK)
Reference temperature, T_0	300	Κ
Reference bulk modulus, K_0	17.822	GPa
Gruneisen parameter, Γ	0.7	
Slope Hugoniot, s	1.79	
Reference bulk sound speed, C_s	3.070	$\rm km/s$
Reference slip rate, $\dot{\gamma}_0$	0.001	ns^{-1}
Slip rate exponent, m	0.1	
Phonon drag slip rate limit	0.0025	ns^{-1}
Hardening matrix, $h_{s_i s_i}$	9.34	MPa
Hardening exponent, a	2.5	
Initial slip resistance g_{s_0}	103.03	MPa
Saturation slip resistance, g_{sat}	155.73	MPa
Artificial viscosity coefficient, C_0	0.1	-
Artificial viscosity coefficient, C_1	1.0	-

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$\overline{C_{11}}$	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}
21.15	10.18	9.77	0.058	4.05	-0.18	20.34	13.35	0.23	6.96	0.14
C_{33}	C_{34}	C_{35}	C_{36}	C_{44}	C_{45}	C_{46}	C_{55}	C_{56}	C_{66}	
21.27	-0.004	5.01	0.19	8.79	0.32	4.16	6.20	0.22	10.00	

Table 3.6. Elastic moduli of β -HMX in GPa (Voigt notation) [130]

3.4.2 Results

3.4.2.1 Collapse of 500 micron diameter void

To compare with the experimental results, simulations of the geometry shown in Figure 3.17 with a void of diameter D=500 μ m were performed, applying an impact velocity of $U_p = 0.1$ km/s. The crystal is impacted along the x- axis which is oriented parallel to the plane normals (010) and (110). Figure 3.19 shows the evolution of the stress σ_{xx} for the case in which the x- axis is parallel to the normal to the planes (010) and (110). The impact generates a compressive stress of magnitude σ_{xx} around 0.6 GPa. Once the wave reaches the void, a tensile wave is generated at its left free boundary. For both crystal orientations, the void reduces its size conserving its circular shape in agreement with previous studies [55]. However, the stress fields are different for the two crystal orientations.

Figure 3.20 exhibits the evolution of σ_{xx} in crystals impacted with $U_p=1.0$ km/s normal to the planes (100), (010) and (110), the deviatoric and volumetric stresses are shown in Figure 3.21 at $t = 0.35 \mu s$. Under these conditions the compressive stress due to the shock is around 9.0 GPa and the void does not conserve its circular shape. A jet is visible in left boundary of the void only for the crystal oriented in the direction (100). The stress patterns are distinct for different orientations, with lower stress fields around the void when the crystal is oriented in the (110) direction.

The velocity field after the shock wave passes through the void is presented in Figure 3.22 for two different crystal orientations and three impact velocities: $U_p = 0.1, 0.5$, and 1.0 km/s. At higher impact velocities the shape of the void does not remain circular. The elastic

moduli for HMX has low anisotropy, see Table 4.2, therefore, there is no noticeable effect of the crystal orientation for lower impact velocities due to limited plastic deformation. As expected, with larger impact velocities the plastic activity increases and the anisotropy of the crystal plasticity model is observed in the velocity and stress fields.



Figure 3.19. Stress field σ_{xx} evolution for crystal with a 500 μ m diameter void, impacted at $U_p = 0.1$ km/s in the direction normal to the planes (010) and (110).

3.4.2.2 Collapse of 10 micron diameter void

The evolution of a 10 μ m diameter void impacted with $U_p = 1.0$ km/s is shown in Figure 3.23. The tress σ_{xx} reaches values of up to 15 GPa around the void. Similarly to the D=500 μ m simulations, the stresses are more symmetric in the (010) case. The temperature field evolution is plotted in Figure 3.24 for the same configurations. The temperature field is more heterogeneous for the case (110) due to the activation of more slip systems.

3.4.2.3 Void collapse rate

To analyze the data with different void diameters and impact velocities, a characteristic time $\tau = D/U_s$ is defined following the work of Wood et al. [55]. This time represents the time it takes the shock to travel the void diameter. The evolution of the void area normal-



Figure 3.20. Stress field σ_{xx} in a crystal with a 500 μ m diameter void impacted with $U_p = 1.0$ km/s normal to the planes (100), (010) and (110).

ized by the initial area, A_0 , is calculated from the simulations as a function of τ , see Figure 3.25. The experimental results with the void area ratio calculated from the images in Figure 3.18 are also shown for comparison. In the simulations, $\tau = 1.5$, the wave travels a distance 1.5D reaching the left edge of the void in Figure 3.17. Therefore, the experimental data is shifted by $\tau = 1.5$. There is very good agreement between the experimental results and the simulations with $U_p=0.1$ km/s. The change in slope for the simulations with $U_p = 0.1$ km/s is due to wave reflections at boundaries.

In Figure 3.25 we plot the normalized pore area versus characteristic time. The solid lines correspond to the crystals impacted on the (110) plane and dashed lines to (010). Even though the plastic activity is different, affecting the shape of the void and temperature, this does not influence the void area ratio evolution significantly, particularly for high U_p . However, the impact velocity has a strong effect with the void area ratio slope increasing



Figure 3.21. (a) Von-Mises stress σ_{vm} and (b) volumetric stress σ_{vol} fields in a crystal with a 500 μ m diameter void compressed wit a piston velocity $U_p = 1.0$ km/s in the direction normal to the planes (100),(010) and (110) at $t = 0.35 \ \mu$ s.

with the impact velocity. The normalized void collapse rate, $\langle A \rangle$, is calculated as the slope of the curves in Figure 3.25 as:

$$\frac{A(t)}{A_0} = -\langle A \rangle \frac{t}{\tau} + b \tag{3.42}$$

The normalized void collapse rate is also calculated from the simulations with D=10 μ m and all the results are summarized in Figure 3.26. As expected, the void size has no significant effect on the normalized void collapse rate given that the plasticity model does not include any size effects. For comparison the molecular dynamics and continuum simulations of Wood et al. [55] in HNS are also included.

3.4.3 Conclusions

This work presents simulations and an experiment of void collapse in HMX with impact velocities from 0.1 km/s to 1.0 km/s. The continuum model is informed from experiments (eos, plasticity) and atomistic simulations (elastic constants) but it is important to emphasize that it has not been calibrated with the experimental results presented here. Due to



Figure 3.22. Velocity field for single crystals with a 500 μ m diameter void impacted along three different orientations.



Figure 3.23. Evolution of the stress field σ_{xx} in single β -HMX crystal with $D=10 \ \mu \text{m}$ diameter void, and compressed normal to two different planes. The impact velocity is 1.0 km/s.

the importance of the dynamics of the void evolution in the resulting temperature field [54], [55], we study the evolution of the void size and its morphology for different crystal orientations and impact velocities. We limit the impact conditions to lower impact velocities and large void size to compare with the experimental results in Figure 3.18. The simulations predict that the area ratio decreases with a slope $\langle A \rangle = 0.1$ in good agreement with the



Figure 3.24. Evolution of the temperature field in single β -HMX crystal with $D=10 \ \mu \text{m}$ diameter void, and compressed normal to two different planes. The impact velocity is 1.0 km/s.



Figure 3.25. Normalized void area versus time for different U_p and crystal orientations with D=500 μ m. The dashed lines correspond to the plane normal (010) and solids lines to (110).

experiments for D=500 μ m and U_p=0.1km/s. Furthermore, the trend in the void collapse rate agrees with previous continuum and atomistic simulations with the void collapse rate increasing with the impact velocity.

While the void size and crystal orientation do not affect the area ratio rate, they strongly affect the void collapse regime and therefore, the temperature. Higher impact velocities



Figure 3.26. Numerical and experimental results of void collapse rates. The black lines are extracted from reference [55].

produce jetting in larger voids. For example, at an impact velocity $U_p = 1$ km/s normal to the plane (100) jetting appears in a 500 μ m void, see Figure 3.22. No jetting is observed for both 10 and 500 μ m voids, impacted at the same velocity and shocked on the plane (010), see Figure 3.23.

Increased plastic activity when the crystal is impacted on the plane (110) renders higher temperature fields. For the 10 μ m void, the maximum temperatures predicted are 472.7 K and 400.5 K for the orientation (110) and (010). These temperatures are not enough to cause any chemical reaction in HMX. Similar simulations with a 1 μ m diameter void and $U_p=1.0$ km/s performed by Austin et al. [49] predict higher temperatures after the collapse of the void. The collision of the jet can generate pressures up to 30 GPa increasing the temperature enough to cause chemical reaction.[47], [49].

Unfortunately, in the regime tested experimentally, with $U_p \sim 0.1$ km/s, the plastic activity is limited. To improve the fidelity of the material model, experiments with larger impact velocity are needed. Extensions of this work will also focus on comparison of temperature fields with atomistic simulations and experiments to investigate the role of voids and other defects in the process of ignition and the transition to detonation.

4. CHAPTER 4: MODELING SHOCKS IN POLYCRYSTALLINE HMX

Preamble

Sections of this chapter will be included in the following paper:

C. A. Duarte, and M. Koslowski. "Computational modeling of polycrystalline β -tetramethylene tetranitramine (β -HMX) under shock compression", In preparation, 2021;

4.1 Introduction

High explosives (HE), such as tetramethylene tetranitramine (HMX), are usually distributed as compacted powders or pellets, which consist of multiple crystals pressed to maximum densities up to 94% [72]. In HMX class III pellets, grains have a size greater than 100 μ m, and cracks or regions with high porosity separate the grains. When β -HMX pellets are shocked, heterogeneous wave propagation paths are formed due to morphological features in the microstructure, such as defects, grain boundaries, and grain orientations. Because of the random grain orientation, rarefaction and recompression waves are formed at the grain boundaries inducing strain localization. The strain localization may lead to the formation of hotspots due to heat dissipation mechanisms such as plastic heating. However, it is still not well understood the role of crystalline anisotropy in forming hotspots, particularly in polycrystalline energetic materials, and how this affects other hotspot formation mechanisms.

There are a few experimental studies of shocks in HMX pellets. Welle et al.[72] studied the ignition behavior of HMX pellets subjected to shock pulses. They observed pellets with small grain size had a lower critical ignition threshold than pellets with large grain size. The pellets with smaller grains had a more extensive interface area which worked as energy localization sites for hotspot formation. Basset and Dlott [64], [132] studied hotspot temperature evolution in shocked ultrafine HMX powder at a flyer impact velocity of 4.3 km/s. In their results, they measured temperature spikes up to 6700 K. They concluded that the magnitude and duration of the spikes depended not only on the chemistry of the explosive but the interaction of the shock wave with the sample microstructure. In a more recent study, Johnson et al. [62] using the same experimental technique, studied hotspot formation in HMX single crystals and polycrystalline grains. They observed that in single crystals embedded in a binder, hotspots formed at corners and edges of the particle. In contrast, for the polycrystalline samples, hotspots formed at grain boundaries and near internal defects and showed higher temperature magnitudes compared to the single crystal case.

On the computational side, several authors have proposed continuum models to study shock-induced hotspots and shock initiation in HE [18], [25], [46]–[48]. Some of these models have also been used to study shock propagation in polycrystalline energetic materials with inclusions [133]–[135], and polymer-bonded explosives (PBX) [136]–[138]. Hardin [135] et al. implemented a mesoscale model to perform 2D and 3D simulations of impact in polycrystalline HMX at velocities ranging from 50 to 400 m/s. The model includes anisotropic elasticity, crystal plasticity, and heating due to plasticity. Their simulations showed that crystal anisotropy dispersed the stress and temperature fields and caused maximum local heating of 32.4 K for impact at 400 m/s. However, the temperature increased solely due to crystal plasticity, and no other heating mechanisms were considered. Other computational models have focused on studying the effect of aluminum inclusions in polycrystalline HMX and PBX. For instance, Chakravarthy and Gonthier [133] implemented a FEM-DEM model to study hot spot formation in granular aluminized HMX. Their model includes hyperelastic-viscoplastic constitutive models. In their simulations, they noticed that Al inclusions enhanced temperature dissipation lowering the ignition sensitivity of the explosive. Later, Miller et al. [134] studied numerically ignition in aluminized PBX under shock loading. The microstructure consisted of bimodal HMX grains and aluminum particles suspended in an Estane binder. They accounted for three forms of heat generation: frictional heating, plastic dissipation in the HMX grains, and viscous dissipation in the binder. They concluded that frictional dissipation between sliding crack surfaces played a much more significant role in developing critical hotspots than plastic deformation. Kim et al. [136] implemented a cohesive finite element model (CFEM) of a polycrystalline HMX with the presence of voids. The model used an elastic-viscoplastic constitutive model and the Birch-Murnaghan EOS. Crystal anisotropy was approximated by changing the elastic modulus of the grains. The presence of voids was modeled by decreasing the stiffness and strength of the material. They concluded that PBX with a small grain size has lower energy thresholds required for ignition from their simulations. Also, the effect of crystal anisotropy did not increase temperature substantially in the materials. Still, it acted as a perturbation to the deformation field, inducing fracture and inelastic deformation and creating critical hotspots. Wei et al. [137] also performed numerical simulations to study the effect of intragranular and interfacial cracks in PBX. They concluded that hotspot density increases with load magnitude and the density of defects. They observed that hotspots formed more readily closed to debonded interfacial sites and that defects lowered the ignition thresholds. However, the effect of material defects on the ignition threshold diminished as the shock strength increased. Recently, Mohan et al. [138] used a crystal plasticity model and an equation of state as implemented in [46] to study shock compression on PBX made of RDX crystals in Estane binder. Crystal anisotropy is captured by assigning different Euler angles to each grain. They observed a strong correlation between the shock temperature and the longitudinal wave speed and Taylor factor for each crystal orientation. Simulations of shock in polycrystalline HMX with realistic microstructures were also recently published. Chun [139] et al. using a machine learning algorithm, generated heterogeneous microstructures of polycrystalline HMX, with different grain morphologies and porosity distributions. They conducted reactive shock simulations using an eulerian model. The simulation results showed that the sample with smaller crystals/voids had a higher density of hot spots in the control volume when compared to the sample with larger crystals/voids.

From the studies previously mentioned, it is clear that crystal anisotropy plays an essential role in the thermo-mechanical response of polycrystalline high explosives compressed at shock velocities. However, we still do not know its effect at different shock strengths and how it affects other hotspot formation mechanisms such as frictional heating. Therefore, this study aims to understand the coupling of crystal anisotropy and fracture in HMX polycrystals and single crystals subjected to sustained shock compression. We use a FE model that includes crystal plasticity and equation of state, fracture, heat conduction, and heat generation due to shock heating, plastic dissipation, frictional heating at cracks. We first performed simulations of sustained shocks in polycrystalline HMX where the grains are perfectly bonded to understand the effect of plastic deformation and hotspot formation due to plastic heating at three different shock strengths. Then, using a phase-field damage model, we simulate shocks in polycrystalline HMX with grain boundaries. Simulations capture fracture evolution and frictional heating at cracks.

4.2 Constitutive model

We used the continuum model for large deformations implemented by Duarte et al. [140] that includes anisotropic elasticity, crystal plasticity, the Mie-Grüneisen equation of state (EOS), fracture evolution, and thermal transport. FE simulations of shocks β -HMX polycrystals are used to study the effect of anisotropic elastoplastic deformation and fracture on the formation of hot-spots.

4.2.1 Crystal plasticity

The crystal plasticity model follows the work in references [46], [115], [140]. and it is based on the decomposition of the deformation gradient into its elastic, \mathbf{F}_{e} , and plastic, \mathbf{F}_{p} , parts:

$$\mathbf{F} = \mathbf{F}_{\mathbf{e}} \mathbf{F}_{p},\tag{4.1}$$

where $det(\mathbf{F}_p) = 1$. The plastic velocity gradient, \mathbf{L}_p , is expressed as the sum of the shear strain rate on each slip system s_i with unit normal $\mathbf{\hat{n}}_{s_i,0}$ and glide direction unit vector $\mathbf{\hat{b}}_{s_i,0}$:

$$\mathbf{L}_{p} = \dot{\mathbf{F}}_{p} \mathbf{F}_{p}^{-1} = \sum_{i=1}^{N_{s}} \dot{\gamma}_{pl,s_{i}} \hat{\mathbf{b}}_{s_{i},0} \otimes \hat{\mathbf{n}}_{s_{i},0}$$
(4.2)

where $N_s = 10$ is the number of slip systems reported in Table 4.1. A power law rule is used to calculate the slip rate [113]:

$$\dot{\gamma}_{pl,s_{i}} = \dot{\gamma}_{0} \operatorname{sign}(\tau_{s_{i}}) \left| \frac{\tau_{s_{i}}}{\tau_{th,s_{i}}} \right|^{1/m}$$
(4.3)

where $\dot{\gamma}_0$ is a reference slip rate, $\tau_{s_i} = 0.5\mathbb{C} : (\mathbf{F}_e^T \mathbf{F}_e - \mathbf{I}) : (\mathbf{\hat{b}}_{s_i,0} \otimes \mathbf{\hat{n}}_{s_i,0})$ is the resolved shear stress on the slip system s_i , and m is the rate sensitivity parameter. \mathbb{C}_{ijkl} is the fourth order elasticity tensor with components shown in Table 4.2. The slip rate in Equation 4.3 is limited by the phonon drag $\dot{\gamma}_{pd}$ when dislocation velocity approaches the shear wave speed following reference [140]. The critical resolved shear stress is obtained using the expression:

$$\tau_{th,s_{\mathbf{i}}} = r_{s_{\mathbf{i}}}g_{s_{\mathbf{i}}} \tag{4.4}$$

where r_{s_i} is the strength ratio in each slip plane (see Table 4.1), and g_{s_i} is the slip resistance that evolves according to the following power law:

$$\dot{g}_{s_{j}} = \sum_{i=1}^{N_{s}} h_{s_{i}s_{j}}\dot{\gamma}_{pl,s_{j}}$$
(4.5)

where $h_{s_i s_j}$ is the hardening matrix [114]:

$$h_{s_{i}s_{j}} = q_{s_{i}s_{j}} \left[h_{0} \left(1 - \frac{g_{s_{j}}}{g_{sat}} \right)^{a} \right]$$

$$(4.6)$$

The parameters h_0 , g_{sat} , and a are the slip system hardening constants and are shown in Table 4.4. These values are assumed to be the same for all slip systems. The expression $q_{s_is_j}$ is called the latent hardening, which defines the hardening of slip system s_i due to slip activity in other slip systems s_j , and it takes the value of 1.0 for coplanar slips systems and 1.4 otherwise [116].

4.2.2 Phase field damage model

In this section we present the phase field damage model (PFDM) used in some of the simulations in this work. In the PFDM, cracks are tracked using a continuum field variable $c(\mathbf{x}, t)$ that represents damaged material if $c(\mathbf{x}, t) = 1$, and intact material if $c(\mathbf{x}, t) = 0$. Several quasi-static and dynamic phase field models of damage have been proposed to study brittle fracture [80]–[83], [141], and they have been extended to ductile materials [84], [85]. In the phase field approximation the crack surface is described by a diffuse Dirac delta function

Slip system	$\mathbf{\hat{n}}_{s_{\mathrm{i}},0}$	$\mathbf{\hat{b}}_{s_{\mathrm{i}},0}$	r_{s_i}
s_1	(010)	[100]	1
s_2	(011)	[100]	0.963
s_3	$(01\overline{1})$	$[\bar{1}00]$	0.963
s_4	$(\bar{1}02)$	[010]	0.933
s_5	(001)	[100]	1.681
s_6	$(\bar{1}02)$	[201]	0.376
s_7	(011)	$[0\bar{1}1]$	0.931
s_8	$(0\bar{1}1)$	$[0\overline{1}\overline{1}]$	0.931
s_9	$(\bar{1}\bar{1}1)$	$[\overline{1}0\overline{1}]$	0.701
s_{10}	$(1\overline{1}\overline{1})$	[101]	0.701

Table 4.1. Slip systems from literature of β -HMX identified experimentally and in MD simulations, with their respective strength ratio r_i as given in [49].

Table 4.2. Elastic moduli of β -HMX in GPa (Voigt notation) [130].

							· · ·	~		L .
C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}
25.10	9.7	12.8	0.0	-1.3	0.0	22.3	11.8	0.0	4.6	0.0
C_{33}	C_{34}	C_{35}	C_{36}	C_{44}	C_{45}	C_{46}	C_{55}	C_{56}	C_{66}	
21.8	0.0	1.4	0.0	9.7	0.0	3.18	11.04	0.0	8.66	

 Table 4.3. Elastic properties used at the grain boundaries.

Symbol	Value	Units
E	24.12	GPa
ν	0.24	-

[86] to replace the integral over the crack surface, Γ_c , [32] by an integral in the volume, Ω_0 . Therefore, the fracture energy can be written as:

$$W_f(c) = \int_{\Gamma_c} G_c ds \approx \int_{\Omega_0} G_c \left(\frac{1}{2l_0} c^2 + \frac{l_0}{2} \left| \nabla c \right|^2 \right) d\mathbf{x}$$

$$(4.7)$$

where l_0 is a length scale parameter that characterizes the thickness of the cracks, and G_c is the critical energy release rate of the material. The elastic part of the free energy

Parameter	Value	Units
Initial density, ρ_0	1.85	g/cm^3
Specific heat capacity, C_v	2357.3	J/(kgK)
Thermal conductivity, k	0.31	W/(mK)
Reference temperature, T_0	300	Κ
Reference bulk modulus, K_0	14.24	GPa
Gruneisen parameter, Γ	0.7	-
Slope Hugoniot, s	2.29	-
Reference bulk sound speed, C_s	2.77	$\rm km/s$
Reference slip rate, $\dot{\gamma}_0$	0.001	ns^{-1}
Slip rate exponent, m	0.1	-
Phonon drag slip rate limit, $\dot{\gamma}_{pd}$	0.025	ns^{-1}
Hardening matrix, $h_{s_i s_j}$	9.34	MPa
Hardening exponent, a	2.5	
Initial slip resistance g_{s_0}	103.03	MPa
Saturation slip resistance, g_{sat}	155.73	MPa
Artificial viscosity coefficient, C_0	0.1	-
Artificial viscosity coefficient, C_1	1.0	-
Plastic dissipation coefficient, β_p	0.5	-
Viscous dissipation coefficient, β_v	0.4	-
Fracture energy HMX bulk, G_c	2.0	$\mathrm{J/m^2}$
Fracture energy grain boundaries, G_c	1.0	$\mathrm{J/m^2}$
Coefficient of thermal expansion, α	$0.214 \cdot 10^{-4}$	K^{-1}
Friction coefficient, μ	0.5	-

Table 4.4. Material properties and model parameters used in the constitutive model for β -HMX crystals [49], [129].

is decomposed into two terms as a function of the Green-Lagrange elastic strain tensor $\mathbf{E}_{e} = \frac{1}{2} \left(\mathbf{F}_{e}^{T} \mathbf{F}_{e} - \mathbf{I} \right)$, the damage phase field c, and the temperature T:

$$W_{\rm e}(\mathbf{E}_{\rm e}, T, c) = W_{\rm e}^+(\mathbf{E}_{\rm e}, T, c) + W_{\rm e}^-(\mathbf{E}_{\rm e}, T)$$
 (4.8)

where $W_{\rm e}^+(\mathbf{E}_{\rm e}, T, c)$ is the integral of the energy density that is degraded by damage and it is given by:

$$W_{\rm e}^{+}(\mathbf{E}_{\rm e}, T, c) = \int_{\Omega_0} (1-c)^2 \psi_{\rm e}^{+}(\mathbf{E}_{\rm e}, T) d\mathbf{x}$$
(4.9)

Note that $\psi_{e}^{+}(\mathbf{E}_{e}, T)$ is multiplied by a quadratic function in terms of the damage field. $W_{e}^{-}(\mathbf{E}_{e}, T)$ is the part of the free energy that is not affected by damage and it is of the form:

$$W_{\rm e}^{-}(\mathbf{E}_{\rm e},T) = \int_{\Omega_0} \psi_{\rm e}^{-}(\mathbf{E}_{\rm e},T) d\mathbf{x}$$
(4.10)

The phase field evolution equation is given by [142]:

$$\frac{\partial c}{\partial t} = -\frac{1}{G_c \eta} \left[-2(1-c)\mathcal{H}\left(\mathbf{X}, t, T\right) + G_c \frac{c}{l_0} - G_c l_0 \nabla \cdot \nabla c \right]$$
(4.11)

where $\mathcal{H}(\mathbf{X}, t, T)$ is the history variable [82] and it is defined as follows:

$$\mathcal{H}(\mathbf{X}, t, T) = \max_{\tau \in [0, t]} \psi_{\mathrm{e}}^{+}(\mathbf{E}_{\mathrm{e}}(\mathbf{X}, \tau), T(\tau))$$
(4.12)

The split of the free energy in Equation 4.8 depends on the material response, several models have been developed to reflect under which conditions cracks nucleate and propagate [141]. In this section we describe the two different damage models used for the grains and the grain boundaries (GBs). We assume that the grains fracture only due to positive volumetric deformation [143] and have a fracture energy of G_c [90]. Therefore, the part of the energy density degraded by fracture contains just the positive volumetric component:

$$\psi_{\mathrm{e}}^{+}(\mathbf{E}_{\mathrm{e}},T) = \psi_{vol}^{+}(J,T) \tag{4.13a}$$

$$\psi_{\mathbf{e}}^{-}(\mathbf{E}_{\mathbf{e}},T) = \psi_{vol}^{-}(J,T) + \psi_{cpl}(\mathbf{E}_{\mathbf{e}},T)$$
(4.13b)

where

$$\psi_{vol}^+(J,T) = \begin{cases} \frac{1}{2}K\delta^2 - K\delta\alpha\Delta T & J \ge 1.0\\ 0 & J < 0 \end{cases}$$
(4.14)

and

$$\psi_{vol}^{-}(J,T) = \begin{cases} \int_{1}^{v/v_0} \sigma_{eos}\left(\xi,T\right) d\xi & J < 1.0\\ 0 & J \ge 1.0 \end{cases}$$
(4.15)

where $K = \frac{1}{9}\mathbf{I} : \mathbb{C} : \mathbf{I}$ is an effective bulk modulus, and $\delta = \frac{3}{2}(J^{2/3} - 1)$. σ_{eos} is calculated using the Mie-Grüneisen EOS and calibrated against atomistic simulations in reference [140]:

$$\sigma_{\text{eos}} = \Gamma \rho_0 C_v \left(T_0 - T \right) \left(\frac{v_0}{v} \right) + \frac{K_0 \chi}{\left(1 - s\chi \right)^2} \left[\frac{\Gamma}{2} \left(\frac{v_0}{v} - 1 \right) - 1 \right]$$
(4.16)

where Γ is the Grüneisen parameter, $\frac{v_0}{v}$ is the specific volume ratio, s is the slope of the Hugoniot curve, and $\chi = 1 - \frac{v}{v_0}$. Note that the pressure σ_{eos} is only used under compression. The coupled deviatoric-volumetric part of the free energy density is obtained from [46]:

$$\psi_{cpl} = \frac{1}{2} \mathbf{E}_{e} : \mathbb{C} : \mathbf{E}_{e} - \mathbf{E}_{e} : \mathbb{C} : \boldsymbol{\alpha} - \left[\frac{1}{2} K \delta^{2} - K \delta \alpha_{v}\right]$$
(4.17)

where α_v is the trace of the thermal strain tensor:

$$\boldsymbol{\alpha} = \frac{1}{2} \left[\exp\left(\frac{2}{3}\alpha(T - T_0)\right) - 1 \right] \mathbf{I}.$$
(4.18)

In some of the simulations, to take into account the different deformation response of the grain boundaries (GBs), we modeled the GBs as a region where no plastic deformation occurs and damage will develop under positive volumetric and deviatoric deformation. Therefore, the split of the energy density in GBs is given by:

$$\psi_{\mathbf{e}}^{+}(\mathbf{E}_{\mathbf{e}},T) = \psi_{vol}^{+}(J,T) + \psi_{cpl}(\mathbf{E}_{\mathbf{e}},T)$$
(4.19a)

$$\psi_{\mathbf{e}}^{-}(\mathbf{E}_{\mathbf{e}},T) = \psi_{vol}^{-}(J,T)$$
(4.19b)

We capture the weak attachment between crystals by reducing the fracture energy at the GBs to $G_c = 1.0 \text{ J/m}^2$. At the moment, there is no experimental work that has investigated the fracture energy between grains in polycrystalline HMX.

4.2.3 Conservation of linear momentum

The equation of balance of linear momentum:

$$\nabla_0 \cdot \mathbf{P} + \rho_0 \mathbf{b} = \rho_0 \ddot{\mathbf{x}} \tag{4.20}$$

where $\mathbf{P} = J\boldsymbol{\sigma}\mathbf{F}^{-1}$ is the first Piola-Kirchhoff stress, **b** is a body force per unit of mass, $\ddot{\mathbf{x}}$ is the acceleration, $J = \det(\mathbf{F}) > 0$, and $\boldsymbol{\sigma}$ is the Cauchy stress tensor. From the free energy function the second Piola-Kirchhoff stress tensor $\mathbf{S} = J\mathbf{F}^{-1}\boldsymbol{\sigma}\mathbf{F}^{-T}$ can be expressed as:

$$\mathbf{S} = (1-c)^2 \frac{\partial \psi_{\mathrm{e}}^+(\mathbf{E}_{\mathrm{e}},T)}{\partial \mathbf{E}_{\mathrm{e}}} + \frac{\partial \psi_{\mathrm{e}}^-(\mathbf{E}_{\mathrm{e}},T)}{\partial \mathbf{E}_{\mathrm{e}}}$$
(4.21)

The volumetric part of the stress is given by:

$$\frac{\partial \psi_{vol}(\mathbf{E}_{e}, T)}{\partial \mathbf{E}_{e}} = \begin{cases} K_{0} J^{2/3} \left(\delta - \alpha_{v}\right) \mathbf{C}_{e}^{-1} & J \ge 1\\ -J \sigma_{eos} \mathbf{C}_{e}^{-1} & J < 1 \end{cases}$$
(4.22)

The coupled deviatoric-volumetric term of the stress is expressed as:

$$\frac{\partial \psi_{cpl}(\mathbf{E}_{e}, T)}{\partial \mathbf{E}_{e}} = \mathbb{C} : (\mathbf{E}_{e} - \boldsymbol{\alpha}) - K_{0} J^{2/3} \left(\delta - \alpha_{v}\right) \mathbf{C}_{e}^{-1}$$
(4.23)

An artificial viscosity tensor is added to the volumetric part of the stress tensor to reduce numerical inestabilities:

$$\mathbf{S}_{vis} = \left(C_0 \rho_0 \frac{\dot{j} \left| \dot{j} \right|}{J^3} h^2 + C_1 \rho_0 c_0 \frac{\dot{j}}{J^2} h \right) \mathbf{I}$$
(4.24)

where h is the element size and c_0 is the longitudinal speed of sound. The coefficient C_0 helps to suppress spurious oscillations behind the wavefront, whereas C_1 spreads the shock front over several elements and lowers the peak amplitude of the oscillations [117], [118].

4.2.4 Heat equation

The time evolution of the the temperature field is calculated from the heat equation:

$$\rho_0 C_v \dot{T} = \Phi - \boldsymbol{\nabla}_0 \cdot \mathbf{q} \tag{4.25}$$

where \mathbf{q} is the heat flux and Φ the mechanical dissipation given by:

$$\Phi = \beta_p \mathbf{S} : \dot{\mathbf{E}}_p + \beta_v \mathbf{S}_{vis} : \dot{\mathbf{E}}_e + \rho_0 T \frac{\partial^2 \psi}{\partial \mathbf{E}_e \partial T} : \dot{\mathbf{E}}_e$$
(4.26)

The first two terms in Equation 4.26 represent heat generation due to plastic and shock dissipation. The coefficients β_p and β_v are included to take into account that only part of the dissipated energy is converted to heat, and they were calibrated from shock simulations in single β -HMX crystals against atomistic simulations et al. [140]. The third term is heat generated due to thermoelastic coupling [46], and it is given by:

$$\rho_0 T \frac{\partial^2 \psi}{\partial \mathbf{E}_{\mathrm{e}} \partial T} : \dot{\mathbf{E}}_{\mathrm{e}} = \rho_0 T \frac{\partial^2 \psi_{\mathrm{eos}}}{\partial \mathbf{E}_{\mathrm{e}} \partial T} : \dot{\mathbf{E}}_{\mathrm{e}} + \rho_0 T \frac{\partial^2 \psi_{cpl}}{\partial \mathbf{E}_{\mathrm{e}} \partial T} : \dot{\mathbf{E}}_{\mathrm{e}}$$
(4.27)

where:

$$\rho_0 T \frac{\partial^2 \psi_{\text{eos}}}{\partial \mathbf{E}_{\text{e}} \partial T} \dot{\mathbf{E}}_{\text{e}} = -\Gamma \rho_0 C_v T \text{Tr} \left(\mathbf{C}^{-1} : \dot{\mathbf{E}}_{\text{e}} \right)$$
(4.28a)

$$\rho_0 T \frac{\partial^2 \psi_{cpl}}{\partial \mathbf{E}_{e} \partial T} \dot{\mathbf{E}}_{e} = -\frac{\alpha T}{3} \exp\left(\frac{2}{3}\alpha(T - T_0)\right) \dot{\mathbf{E}}_{e} : \mathbb{C} : \mathbf{I} + K\alpha T J^{2/3} \exp\left(\frac{2}{3}\alpha(T - T_0)\right) \operatorname{Tr}\left(\mathbf{C}^{-1} : \dot{\mathbf{E}}_{e}\right)$$
(4.28b)

The heat flux is:

$$\mathbf{q} = k\nabla_0 T + \mathbf{q}^c \tag{4.29}$$

The last term in Equation 4.29 is the heat flux generated due to frictional sliding at crack surfaces and can be calculated from the following expression [88]–[90]:

$$\mathbf{q}^{c} \cdot \mathbf{n}^{c} = -\mu \left\langle -t_{n} \right\rangle v^{s} \tag{4.30}$$

where μ is the friction coefficient, $\mathbf{n}^c = \nabla c / \|\nabla c\|$ is the normal vector to the crack, $t_n = \mathbf{n}_i^c \boldsymbol{\sigma}_{ij} \mathbf{n}_j^c$ is the normal component of the traction vector at the crack surface, and v^s is the magnitude of the sliding velocity between the two surfaces of the crack. The symbol $\langle \rangle$ in Equation 4.30 ensures that heat is generated only when the traction is negative, i.e. when the cracks are in compression. It is important to mention that the friction coefficient μ determines the magnitude of heat generated due to friction. Experimentally, this coefficient has been estimated to vary between 0.3-1.0 [37], [91], [144] for HMX crystals. Therefore, we used a value $\mu = 0.5$ in all simulations.

4.2.5 Numerical implementation

The constitutive models described in the previous sections as well as the equations of conservation of linear momentum (see Equation 4.20), conservation of energy (see Equation 4.25), and damage evolution (see Equation 4.11) were implemented in the multiphysics finite element software MOOSE [145]. To solve the system of equations, we used a Jacobian-free Newton-Krylov technique [146]. The Newark time integration scheme [147] is used to calculate the inertia term in Equation 4.20. The material parameters used in the simulations are included in Table 4.4.

4.3 Results

We present 2D plane strain simulations of a compressive shock wave traveling in a β -HMX polycrystal with the geometry and boundary conditions shown in Figure 4.1. The grains were built using a Voronoi tessellation algorithm with an average grain size of 250 μ m. We assign different Euler angles (ϕ, θ, ψ) randomly from a uniform distribution to each grain, see Figure 4.2. Piston velocities $U_p = 0.1, 0.4, \text{ and } 1.0 \text{ km/s}$ along the X direction are applied on the left surface and fixed boundary conditions ($u_y = 0$) on the top and bottom boundaries, as well as and on the right boundary $(u_x = 0)$. Comparisons of the temperature over the line $Y = 250 \ \mu m$ for different average sizes is shown in Figure 4.3. Using triangular elements with an average size of $h = 10 \ \mu m$ the temperature field in the polycrystal appears to be well resolved in these simulations.



Figure 4.1. Geometry and boundary conditions of polycrystalline HMX. The grains 1 and 2 are indicated in the geometry.



Figure 4.2. Euler angles (ϕ, θ, ψ) fields.

4.3.1 Polycrystalline β -HMX

The model used in this section includes anisotropic elasticity and crystal plasticity, the EOS, and the heat equation. Damage evolution and frictional heating are not taken into account to study only the effect of anisotropic crystal plasticity in the temperature field. Figures 4.4(a) and (b) show contour plots of temperature and accumulated plastic shear slip, $\gamma_p = \sum_{i=1}^{N_s} \int_t |\dot{\gamma}_{s_i}| dt$, in the polycrystal shocked with piston velocities $U_p = 0.1, 0.4$ and 1.0 km/s. A heterogeneous temperature field is observed when the shock wave travels due to the different responses of the grains with various orientations. Within the polycrystal, the temperature reaches a maximum magnitude of 310 K, 352 K, and 461 K, for piston velocities $U_p = 0.1$ km/s, 0.4 km/s, and 1.0 km/s, respectively. The grains that have the largest magnitude of accumulated plastic slip also show the highest temperature. The orientation of these grains favors plastic deformation for shocks along X, and consequently, they have more plastic work dissipated as heat (see the second term in Equation 3.37). The large temperatures observed at the left boundary in Figure 4.4(a) are caused by the use of artificial viscosity. This numerical artifact is known as wall-heating [148], and therefore, we do not consider temperature values in this region in our analysis.



Figure 4.3. Results of mesh sensitivity analysis showing the temperature vs position in X using meshes with different element size, for shocks at (a) $U_p = 0.1 \text{ km/s}$ at $t = 0.4 \mu \text{s}$, (b) $U_p = 0.4 \text{ km/s}$ at $t = 0.4 \mu \text{s}$, and (c) $U_p = 1.0 \text{ km/s}$ at $t = 0.1 \mu \text{s}$.

For comparison, we also performed shock simulations in single crystals with the orientation of the grains labeled as 1 and 2 in Figure 4.1. Their Euler angles are reported in Table 4.5. These orientations are chosen because these grains undergo small and large amounts of plastic deformation compared to the other grains in the domain. The single crystal with orientation 2 (SO2) shows a larger temperature increase than the single crystal with orientation 1 (SO1), as shown in Figure 4.5 (a) and (b). As expected, the temperature field is homogeneous in the single crystal simulations, and the temperature jump is sharper as the impact velocity increases. The maximum temperature in the sample SO1 is 308 K for $U_p =$ 0.1 km/s, 339 K for $U_p = 0.4$ km/s, and 432 K for $U_p = 1.0$ km/s. In the case of SO2, the maximum temperature is 309 K for $U_p = 0.1$ km/s, 343 K for $U_p = 0.4$ km/s, and 458 K for $U_p = 1.0$ km/s.

 Table 4.5. Euler angles of single crystals 1 and 2.

 Crystal $\phi(^{\circ})$ $\theta(^{\circ})$ $\psi(^{\circ})$

Crystal	$\phi(^{\circ})$	$ heta(^\circ)$	$\psi(^{\circ})$
1	61.97	-14.15	9.22
2	83.19	-40.34	61.65

Figure 4.6 shows a comparison of the temperature versus position in X along the line $Y = 250 \ \mu m$ for the polycrystal (RO) and single crystals SO1 and SO2. Temperature spikes are observed in the grain boundaries for RO, see Figure 4.6, surpassing the temperatures in the single crystals. The temperature distribution is analyzed in Figure 4.7. These plots present the area, A, with a temperature equal to or greater than a temperature value T. Higher temperature is observed in the polycrystal for all U_p . However, at $U_p = 1.0 \ \text{km/s}$, the temperature distribution in RO is closer to the one in SO2 (see Figure 4.7 (c)) confirming that the effect of crystal anisotropy is less important for stronger shocks since most of the stress magnitude comes from the EOS. Additionally, the orientation of single crystal SO2 favors plastic deformation, and therefore the plastic dissipation in SO2 is higher than the polycrystalline sample and single crystal SO1.



Figure 4.4. (a) Temperature and (b) accumulated plastic shear slip γ_p contour plots in polycrystalline HMX undergoing shock loading at piston velocities $U_p = 0.1, 0.5, \text{ and } 1.0 \text{ km/s}.$



Figure 4.5. Temperature contour plots for (a) single crystal 1 and (b) single crystal 2, shocked at piston velocities $U_p = 0.1, 0.5, \text{ and } 1.0 \text{ km/s}.$

4.3.2 Polycrystalline β -HMX with dynamic fracture

The model used in this section includes anisotropic elasticity and crystal plasticity, the equation of state, the phase field damage model, and the heat equation, including dissipation due to friction at cracks. We perform 2D plane strain shock simulations on the polycrystalline β -HMX domain shown in Figure 4.8. The sample is loaded applying piston velocities $U_p = 0.1$, and 0.4 km/s on the left boundary along the X direction, as shown in Figure 4.8. Fixed boundary conditions are used in the other surfaces. The grain boundaries (GBs)



Figure 4.6. Temperature vs position in X along the line $Y = 250 \ \mu m$ in shocked HMX polycrystal (RO), single crystal 1 (SO1), and single crystal 2 (SO2).



(a) $U_p=0.1 \text{ km/s}, t=0.4 \mu \text{s}.$ (b) $U_p=0.4 \text{ km/s}, t=0.4 \mu \text{s}.$ (c) $U_p=1.0 \text{ km/s}, t=0.25 \mu \text{s}.$

Figure 4.7. Comparison of the area exceeding temperature T for shocked HMX polycrystals (RO), single crystal 1 (SO1), and single crystal 2 (SO2) for different piston velocities U_p .

shown in red have a different material model as explained in Section 4.2.2. The orientation of the grains in the polycrystal is the same from Figure 4.1 (b).

Figures 4.9 (a) and (b) show the temperature contour plots for shocks at $U_p = 0.1$ and 0.4 km/s for the polycrystal sample including fracture (RO+F), both at time 0.4 μ s. The shock through the polycrystal generates damage at the GBs and heat dissipation due to plasticity and friction at cracks. The fracture model used at the GBs considers damage due to shear deformation, and therefore cracks nucleate at these regions. In contrast, no intragranular cracks are formed in the sample since the fracture model used in the bulk of the crystal considers damage evolution only under positive volumetric deformation. Note that in Figure 4.9, GBs oriented close to 45° from the shock direction show the highest temperatures due to shear. A comparison of the temperature over the line $Y = 250 \ \mu$ m for the polycrystal with damage (RO+F) and without (RO) is shown in Figure 4.10. The maximum temperature difference between RO and RO+F is 25 K for $U_p = 0.1 \text{ km/s}$ and 125 K for $U_p = 0.4 \text{ km/s}$, approximately. Additionally, the temperature in the grains is higher also in the interior due to heat diffusion.

We also perform simulations with all the grains oriented in the same direction to understand the influence of the grain orientation on fracture and friction at GBs. We choose all the grains oriented in the direction of grains 1 and 2 shown in Figure 4.1. The temperature fields are shown in Figures 4.9 (a) and (b) for samples with grains oriented in the direction of crystal 1 (SO1+F) and crystal 2 (SO2+F). Fewer hot-spots are formed in the samples SO1+F and SO2+F compared to RO+F. Furthermore, the temperatures at GBs are lower in the samples with grains oriented in the same direction than in the polycrystal with grains oriented randomly. The maximum temperature in the polycrystal RO+F is 3.25 K higher than the single crystal cases for $U_p = 0.1$ km/ and 22.4 K for $U_p = 0.4$ km/s (see Figure 4.11(b)). Larger stress concentrations at GBs appear when grains are oriented in different directions due to impedance mismatch between grains. The temperature distributions, including frictional heating, are shown in Figure 4.11. We also added the temperature distribution of the polycrystal without the fracture (RO). Figure 4.11 shows that including fracture and friction heating can increase the local temperature by 10 K for $U_p = 0.1$ km/s and by by 150 K for $U_p = 0.4$ km/s, approximately. Although the random crystal orientation in the shocked samples increases their temperature, the magnitude of temperature increase is small. It may not be negligible, especially at larger impact velocities than the ones under study.



Figure 4.8. HMX polycrystal with grain boundaries in red.



Figure 4.9. Temperature contour plots in shocked polycrystalline HMX with grains oriented randomly (RO+F), single orientation 1 (SO1+F), and single orientation 2 (SO2+F).


Figure 4.10. Temperature vs X along the line $Y = 250 \ \mu \text{m}$ for polycrystalline HMX with (RO+F) and without fracture (RO).



(a) $U_p = 0.1 \text{ km/s}, t = 0.4 \mu \text{s}$ (b) $U_p = 0.4 \text{ km/s}, t = 0.4 \mu \text{s}$

Figure 4.11. Comparison of the area exceeding temperature T for shocked polycrystalline HMX samples without fracture (RO), with fracture (RO+F), and all grains with the orientations of single crystals 1 (SO1+F) and 2 (SO2+F).

4.4 Summary and conclusions

In this paper, we presented shock simulations in polycrystalline β -HMX to study the effect of crystal anisotropy on hotspot formation. Firstly, in section 4.3.1, we ran shock simulations without fracture nor frictional heating to study only dissipation due to crystalographic slip. The results showed that due to crystal anisotropy, heterogeneous temperature fields formed with the passage of the shock. In the polycrystal, the grains that get warmer also show higher magnitudes of accumulated slip. In contrast, the temperature field is more homogeneous for shocks in single crystals, and the amount of plastic dissipation is controlled by the crystal's orientation with respect to the shock direction. As the shock strength increases, the magnitude of plastic dissipation also increases since more crystallographic slip is present. Nevertheless, for none of these shock configurations, the temperature would be high enough to cause the chemical decomposition of the energetic material [149].

Secondly, to include the effect of fracture and heating due to friction at cracks, we ran the simulations with the constitutive model explain in Section 4.3.2. Fictional heating becomes the dominant hotspot formation mechanism when damaged, and weak GBs are included in the simulations. As the crystals' interfaces break and crack surface sliding occurs, temperature increases due to friction at cracks and varies approximately 12 K and 125 K for piston velocities $U_p = 0.1$ km/s, and 0.4 km/s, respectively. Hotspots tend to form at damaged GBs oriented 30-60° from the shock direction. In this type of simulations, crystal anisotropy does not play an important role in temperature generation due to plastic dissipation. However, the random orientation of the crystals creates heterogeneous deformation and stress fields that cause the formation of a higher number of hotspots than the observed in the samples where all the grains are oriented in the same direction (see Figure 4.9(a) and (b)). Furthermore, as it can be seen in Figure 4.11 (a) and (b), for both cases of U_p , the sample with grains randomly oriented (RO+F) shows the highest temperatures. This situation occurs as a result of the higher degree of impedance mismatch between crystals in the R0+F, which facilitates the formation of higher gradients of stress and velocity at the GBs.

Although frictional heating is the most critical hotspot formation mechanism in the present shock simulations, atomistic and continuum simulations have shown that the collapse of voids can also cause a significant temperature increase in EMs [126], [140]. We performed shock simulations in a single crystal containing a single void with diameter $d = 20 \ \mu \text{m}$ and $40 \ \mu \text{m}$ (see Figure 4.12) using the same constitutive model described in Section 4.2.1 for β -HMX. Temperature contour plots are shown in Figure 4.13 showing temperature localization around the void due to plastic dissipation. A comparison of temperature distribution over the

area for the simulations of single crystals with voids and the polycrystals is shown in Figure 4.14 (a) and (b). Higher temperatures are observed in the single crystals compared to the polycrystal HMX. Temperature localizes in smaller areas in the single crystals compared to the polycrystals. Furthermore, a few hotspots form around the void generated due to plastic dissipation, whereas in the polycrystal, several hotspots are formed as shown in Figure 4.15. This situation suggests that including porosity and simulating heat generation due to the collapse of several voids in the present simulations could lead to hotter and bigger hotspots, increasing the sensitivity of polycrystalline explosives significantly. Future work should focus on studying the effect of the collapse of voids which could be present both at the bulk of the crystal and in the GBs of an β -HMX polycrystal.



Figure 4.12. Geometry and boundary conditions of single HMX crystal with a void of diameter d.



Figure 4.13. Temperature contour plots of shocked single crystals containing a void of diameter d at times $t = 0.015 \ \mu s$ for $d = 20 \ \mu s$, and $t = 0.030 \ \mu s$ for $d = 40 \ \mu s$.



Figure 4.14. Comparison of the area exceeding temperature T for shocked single crystal SO2 containing a void with diameter d, and polycrystalline HMX samples with random grain orientation without fracture (RO),random grain orientations with fracture (RO+F), and all grains with the orientations of single crystal 2 (SO2+F). The distributions are obtained for (a) Voids at $t = 0.015 \ \mu$ s, and polycrystals at $t = 0.4 \ \mu$ s, and (b) voids at $t = 0.030 \ \mu$ s, and polycrystals at $t = 0.4 \ \mu$ s.



Figure 4.15. Hotspots size d_c vs temperature for shocked single crystal SO2 containing a void with diameter d, and polycrystalline HMX ith fracture (RO+F), and all grains with the orientations of single crystal 2 (SO2+F). The hotspots are obtained for (a) Voids at $t = 0.015 \ \mu$ s, and polycrystals at $t = 0.4 \ \mu$ s, and (b) voids at $t = 0.030 \ \mu$ s, and polycrystals at $t = 0.4 \ \mu$ s.

5. CHAPTER 5: SUMMARY

In this work, through computational modeling and simulations, we study the response of single crystals and polycrystals made of β -HMX, subjected to dynamic loading such as impact, shocks, and harmonic excitation. In Chapter 2 we study dynamic fracture and hotspot formation in β -HMX grains embedded in Sylgard binder undergoing high strain rate compression and harmonic excitation. To model fracture, we present simulations using the phase field damage model (PFDM). Furthermore, we implement a thermal model to capture temperature increase due to fracture dissipation and frictional heating at cracks and debonded HMX/Sylgard interface. The effect of impact velocity and crack density in the HMX grains is addressed. Simulations showed that cracks developed parallel to the impact direction due to transversal expansion of the HMX particles, as seen in kolsky bar experiments in HMX crystals performed at Purdue University. Crack patterns are strongly dominated by initial defects such as preexisting cracks and interface debonding. Additionally, crack branching was observed when the impact velocity increases above 100 m/s. Regions with initial debonding between HMX particles and the polymer are critical sites where cracks nucleate and propagate. Heating due to friction generates in these regions. Our simulation results indicate that a frictional heating mechanism may be sufficient for ignition at an impact velocity of 400 m/s or above.

We also looked at the effect of crack density in the HMX particles. We observed that although cracks affect the sensitivity to ignition, the temperature increase is much higher at debonded particle/binder interfaces. Simulations of a pristine particle under dynamic high-frequency harmonic excitation show that damage starts at the particle/binder interface. The preferential locations are where the stress wave first impacts the particle or in the vicinity of defects. As expected, higher frequencies and larger amplitudes lead to an increase in the damage growth rate. Initial defects in the particle and cracks at the interface are added to quantify their effect. Adding these defects reduces the time for damage growth and consequently augments heat generation due to friction. The simulations suggest that the intensity of the thermal localization can be better controlled by modifying the bonding properties between the particle and the binder rather than reducing the content of bulk defects in the particle.

In Chapter 3 we present simulations of shock compression in β -HMX single crystals. For this purpose, we implemented a constitutive model that simulates the anisotropic response of this type of energetic crystal. The model includes a rate-dependent crystal plasticity model and the Mie-Grüneisen equation of state to obtain the pressure due to shock. Temperature generates in the material due to plastic dissipation, shock, and thermo-elastic coupling. The model is calibrated with non-reactive atomistic simulations, courtesy of Professor Strachan's group, to ensure the model obeys the Rankine-Hugoniot jump conditions. We compare finite element (FE) and molecular dynamic (MD) simulations of the collapse of an 80 nm size void in a β -HMX crystal subjected to different shock strengths. The crystal is shocked, normal to the crystallographic plane (010). The FE simulations captured the transition from viscoelastic collapse for relatively weak shocks to a hydrodynamic regime at strong shocks, the overall temperature distributions, and the rate of pore collapse. However, MD simulations exhibit more localization of plastic deformation due to nano shear banding, a mechanism that our model does not capture. The void collapse rate and temperature field are strongly dependent on the plasticity model in the FE results, and we quantify these effects. We also studied the collapse of a micron size void in HMX impacted at different crystal orientations and impact velocities. The simulation results of void collapse are in good agreement with the gas gun experiment for void with size $D = 500 \ \mu m$ and $U_p = 0.1 \ km/s$. While the void size and crystal orientation do not affect the area ratio rate, they strongly affect the void collapse regime and temperature. Higher impact velocities produce jetting in larger voids. Also, increased plastic activity when the crystal is impacted on the plane (110) renders higher temperature fields.

In Chapter 4, we studied shock compression and dynamic fracture in polycrystalline HMX. We used the same continuum model developed for single crystals in Chapter 3. These studies aim to understand the role of crystal anisotropy and its effect on other hotspot formation mechanisms such as frictional heating. We first performed simulations of sustained shocks in polycrystalline HMX, where the grains are perfectly bonded to understand the

effect of plastic deformation and hotspot formation due to plastic heating. Then, using a phase-field damage model, we simulate shocks in polycrystalline HMX with grain boundaries. Simulations capture fracture evolution and frictional heating at cracks. In the polycrystalline case, we study heat generation due to shock and plastic deformation. A heterogeneous temperature field forms when the shock wave travels in the material. Temperature increases more in crystals that showed a higher magnitude of accumulated slip γ_p . When damage and weak grain boundaries are included in the simulations, frictional heating becomes the dominant hotspot formation mechanism. As the crystals' interfaces break and crack surface sliding occurs, temperature increases due to friction at cracks. Hotspots tend to form at cracks oriented 45° from the shock direction. For this case, crystal anisotropy does not play an important role in temperature generation due to plastic dissipation. However, the random orientation of the crystals creates heterogeneous deformation and stress fields that cause the formation of a higher number of hotspots than the case where all the grains are oriented in the same direction.

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