3.2 Combustion and Energetic Materials

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Overview

Combustion of solid propellant composed of energetic materials is the driving thermomechanical force in the operation of a solid rocket motor. Accurate modeling and simulation of the combustion and resulting regression of solid propellants entails research activities in several areas, including the description and propagation of the propellant combustion interface, modeling of solid propellant flames, combustion instability analysis, and constitutive modeling of energetic materials.

Propellant Combustion and Flame Modeling

Modeling Heterogeneous Propellant Combustion (Buckmaster, Jackson, and Massa)

Rocfire is a CSAR tool built to analyze the burning characteristics of heterogeneous solid propellants. The goal is an unsteady three-dimensional simulation of heterogeneous propellant burning that can be used to generate a subgrid combustion model for the CSAR system integrated code.

One accomplishment this past year was the development of a new three-step kinetic model for the combustion processes in the gas phase. For validation, burning rate simulations were carried out for Miller packs SD-III-03 and SD-III-24. The propellant morphology for each pack was computed using Rocpack, an in-house particle packing code. Figure 3.2.1 shows a typical pack, while Figure 3.2.2 are level surfaces of the total heat output in the gas phase. Figure 3.2.3 depicts the experimental burning rates Miller observed, as well as the simulated results from Rocfire. Each data point derives from a computer run on ASCI Blue Pacific using 25 processors and took about four wall clock hours. The experimental values of Miller are shown as circles, the numerical results from our previous two-step kinetic scheme are shown as squares, while the new results using the three-step kinetic scheme are shown as asterisks. Note the overall improvement between the experimental results and the numerical results for the three-step scheme. Future work will focus on generating reduced kinetic mechanisms appropriate for heterogeneous propellants. Future work will also focus on further development and validation of Rocfire, and relevant modeling and physics issues.

Fig. 3.2.1: Rocpack packing simulation for Miller SD-III-17.

Fig. 3.2.2: Rocfire simulation of burning heterogeneous propellant. Flame colors represent total heat output in gas phase above corrugated surface – red hottest, blue coolest.
Modeling Aluminized Propellant Combustion Using Level Sets (Wang, Jackson, and Massa)

Current work is being carried out using level-set technology to remove the restriction of the representation of the surface by a mapping function. This allows the surface to develop complex shapes, as would be expected when, say, aluminum particles are present, when the pack is fuel rich, or when surface cracks are present. Preliminary results show good agreement between the current solver Rocfire and the present method when the surface is single-valued. The level set code has recently been extended to include particle dynamics; see Figure 3.2.4. In this figure a single aluminum particle, shown just before detachment, becomes exposed to the hot gases as the surface regresses. When the particle detaches from the surface, its subsequent motion is determined by particle dynamics. Future work will focus on further development of the code, its extension to three-dimensions, the modeling of agglomeration processes, melt layers, radiation, etc. Comparisons to existing experimental work will be done whenever appropriate.

Solid Propellant Ignition Theory and Validation (Weber, Tang, and Brewster)

Simulation and experimental validation of radiant ignition of an AP-composite propellant, specifically RSRM space shuttle propellant, has been accomplished. The simulation used a surface temperature ignition model. The experimental validation used a CO$_2$ laser and RSRM propellant. Figure 3.2.5 shows a sequence of images of the ignition process. It can be seen that ignition is localized and possibly occurs at a hot spot in association with an aluminum particle. The ignition criterion used is the classical Go/No-Go method. By this method the laser flux is turned on for a specific pulse duration, which is varied. If the pulse duration is below a threshold (ignition) value, the propellant does not ignite. Above this threshold the propellant ignites and continues to burn even though the laser is turned off. Figure 3.2.6 shows the experimental results obtained at UIUC for RSRM propellant and at ONERA for a similar composite propellant. As always occurs, the ignition time decreases as laser flux increases.

The simulation result is also plotted in Figure 3.2.3 and demonstrates excellent agreement with the experiments. Two specific findings came from this study: (1) RSRM propellant ignition temperature is approximately 600 K, and (2) it is necessary to include in-depth absorption of radiation to get the correct ignition time versus flux variation or slope. A three-flux method was implemented to solve...
the radiative transfer equation with anisotropic scattering particles including large AP, small AP, Al, and Fe$_2$O$_3$ to obtain the propellant optical properties. The equivalent isotopic extinction coefficient and albedo for a mixture consisting of multi-component anisotropic scattering particles was derived. The effect of the optical properties and phase function of individual component is accounted for. The reflectivity of the shuttle propellant at wavelength of 10.6 µm (CO$_2$ laser) has been calculated. The calculated result is in good agreement with that estimated from radiant ignition experiments. Important qualitative findings were also made regarding the difference between ignition behavior at high- versus low-flux conditions. In spite of the physical complexities of the ignition process, the model was able to successfully capture the correct variation of ignition time with flux magnitude. Convective heat transfer was also added to the model and experimental validation efforts begun during the past year.

Modeling was begun in collaboration with the Fluids Group to simulate the radiative heat feedback resulting from the optically thin region of burning aluminum droplets and molten aluminum oxide particles in the aluminum-distributed combustion flow field near the propellant surface. The results will be used in a radiant ignition model and solid propellant combustion model.

Future plans: The results so far have shown that although the homogeneous surface temperature model seems to work reasonably well for predicting ignition of composite propellants, the process is still highly localized and is three-dimensional. Accordingly a new effort will begin to do full, three-dimensional Monte Carlo simulation of radiative energy transport in composite propellants with the goal of predicting the localization of the ignition event. In addition, the experimental validation effort will be expanded to include radiation with a spectral distribution that is more representative of that found in the igniter products of a solid rocket motor, namely, near-infrared radiation.
Multi-dimensional Flame Structure and Propellant Regression Rate Simulation and Validation (Fitzgerald and Brewster)

A laminate propellant configuration is being used to develop and validate kinetics and other modeling assumptions for AP/hydrocarbon composite solid propellant combustion. One major accomplishment this year was confirmation that lateral boundary conditions do not affect the inner flame and surface structure for propellants that are overall stochiometrically balanced or fuel-lean (over-ventilated in the Burke-Schumann sense). This is important because of concerns that had been raised about the validity of experimental comparisons with single-layer laminates and the applicability of those results to composite propellants, which are more like periodic boundary conditions. Figure 3.2.7 shows three computational simulations (a-c) and three experimental validations (d-f) for comparison. The pressure is 13 atm and the fuel layer (pure binder) thickness is 130 µm. In (a-c) the amount of oxidizer present as outer AP layers is increased such that the sample goes from being slightly fuel-lean (over-ventilated) in (a) to highly over-ventilated in (c). The protrusion of the binder stays relatively constant while the height of the outer AP walls increases as expected. Figure (d) shows a triple fuel-layer laminate experimental result, which corresponds approximately to periodic boundary conditions as calculated in (a). The agreement between the predicted binder and AP protrusions in (a) and the experimental results in (d) is encouraging. Figures 3.2.7 (e-f) are for single fuel layer samples with increasing outer AP thickness. Both the simulation results (b-c) and the experimental results (e-f) show that the outer AP protrusion increases with increasing excess oxidizer and the high-temperature gas zone moves toward the surface. Moreover, in spite of this expected trend with increasing outer AP, the degree of binder protrusion is relatively constant, unaffected by the lateral boundary conditions, as attested by both simulations and experiments. In this way the use of single-layer laminates has been shown to be a viable option for experimental validation of the model as long as fuel-rich conditions are avoided, and a useful framework is defined for refining our modeling assumptions.

Future plans: There is a continuing need for further validation by comparison between simulations and experimental results, particularly for oxygenated fuel conditions. Only a small number of comparisons have actually been done thus far. We will continue focusing on comparisons between simulations and experiments and thereby refining model assumptions. A continuing shortcoming of the current model is the inability to correctly predict protrusion of fuel for oxygenated binders with wide fuel thickness and/or high pressure, which deficiency has its origins in thermochemical and kinetics assumptions used. We will work to correct this deficiency.
Thermo-mechanical Modeling of Solid Propellant Flames (Stewart and Kuznetsov)

We are examining the thermo-mechanical structure of the propellant flames in order to better understand the influence of thermal expansion in the narrow layer close to the surface of the propellant, and the effects that are introduced by curvature of the burning surface. This will improve the simplified models of propellant combustion interface used in large-scale computer simulation of solid rocket motors. Our approach consists of analytical study and numerical experiment.

Recently, an explicit surface curvature correction to the regression rate for arbitrary surface geometry was derived. Figure 3.2.8 shows a comparison between this asymptotic result and numerical solution of the corresponding ODE in spherical and cylindrical geometry, for HMX deflagrating with the surface temperature $T_s = 700K$. In the limit of high Damkohler number and low activation energy in the gas, a solid-controlled combustion of spherical propellant particle (void) in hot atmosphere was solved analytically. Next year, work in this direction will be continued to combine effects of thermal expansion and surface curvature within one simplified deflagration model.

Along with analytical effort, we will continue to simulate solid propellant combustion of an arbitrarily shaped solid propellant surface. Tracking of the surface position will be performed by a fast tube (or banded) level-set method. The solid phase is to be modeled by a 2-D version of the nonlinear heat equation that includes thermal expansion effects. For the gas phase, we are using the low Mach number solver \textit{PLAMYA2D}. Currently extensive tests of the one-dimensional version of the coupled code are being performed.

Finally, we will collect all results and make a comparison of the theoretical modeling and numerical simulation, which will result in the choice of the best available model for enhanced regression rate suitable for use in surface deflagration simulation at CSAR.

Combustion Simulations

Using \textit{Rocfire} as Subgrid Component of Rocket Simulations (Massa, Buckmaster, and Jackson)

The objective of this work is to incorporate subgrid combustion ingredients into large-scale solid-propellant rocket simulations in a rational fashion. This is a challenging problem because the numerical grid for the chamber flow might be measured on the centimeter scale, whereas that for the combustion simulations is on the micron scale. Thus, the combustion simulations are subgrid ingredients of the chamber simulations, and evaluation of their macroscopic contribution is nontriv-

![Fig. 3.2.8: Curvature effects on regression rate for spheres and cylinders of HMX.](image)

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![Fig. 3.2.9: Results for pressure rise (left) and pressure pulse (right).](image)

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ial. The analysis begins by spatially averaging the heat equation within the solid to generate a one-dimensional equation with a number of source terms defined by the multidimensional thermal field and surface corrugations. Each of these terms is evaluated numerically, and those that may be neglected are identified; models are defined and tested for those that may not. Closure of the one-dimensional description is achieved by relating the mean surface regression rate and the heat flux from the combustion field at the surface to the pressure and the average surface temperature. These relations are in the form of a look-up table generated from Rocfire, the in-house multidimensional simulation code. Comparing the predictions with those of the exact model tests the accuracy of the one-dimensional system. Figure 3.2.9 shows a comparison between the exact (wiggly) with those of the one-dimensional model (dash); quasi-steady results are also shown (symbols). Future work will consider further refinements of the model and the incorporation of the model into full-scale rocket simulations.

RSRM Burnback Simulation (Tang, Ross, Yoo, Stewart, and Brewster)

Development of a reduced-equation model for simulating RSRM full-scale burnback was begun. The goal is to be able to simulate normal RSRM operation including propellant burnback using reduced physical submodels that retain essential physics for normal motor simulation. The purpose is to develop a capability that can augment the multiphysics integrated code by filling the gaps between detailed simulations, gaps that can’t be covered by the full-physics code due to computational limitations. The governing equations for fluid dynamics have been derived and will be solved by an existing flow solver AXS1D. The propellant grain will be represented in 3-D and its burnback will be modeled by the level-set code WAVETRACKER.

Combustion in Cracks (Short, Liu and Kessler)

This work involves both the modeling and three-dimensional DNS of combustion in and flame spread through small cracks in homogeneous and heterogenous propellants. The project aim is to reproduce via simulation a series of on-going experiments at DOE LANL by L. Berghout, S. Son and B. Asay that have been designed to elucidate both the dynamics of combustion that occurs in small cracks formed in energetic materials, as well as combustion-induced crack propagation.

![](image)

Fig. 3.2.10: Energy of various structure of interest as function of volume. Energetics of molecular structures are plotted for comparison. CG and HPC structures are very close in energies in region where transition would be expected. Slope of line tangent to both epsilon and CG structure give estimated transition pressure of 54 Gpa.
ward a full 3D simulation of the LANL experiments. Currently Rocflu is being extended to deal with reactive flows. This will allow a verification of many elements of the full GENx code with detailed experimental data.

**Energetic Materials**

**Path Integral Monte Carlo Simulations of Hot, Dense Matter (Ceperley and Esler)**

We have further developed, tested and applied to dense hydrogen, better methods for *ab initio* simulation. We have demonstrated that the newly devised “Coupled Electronic-Ionic Monte Carlo” method is efficient for calculations of warm dense matter such as occurs in combustion (Figure 3.2.11). We have developed novel forms for the wavefunction of hot dense hydrogen, allowing much more accurate calculations, particularly at lower temperatures. Novel Monte Carlo methods have been developed that allow us to go easily from the bonding to the plasma state of dense hydrogen. We performed simulations of molecular and metallic hydrogen in the temperature range of 300-1000K without assuming an intermolecular potential or a density functional for the electrons and including effects of zero-point motion. Further, we have developed a new method and codes to eliminate core electrons and are testing these pseudo-potentials on heavier elements. To this end we are developing a new object oriented code in C++ to perform a variety of quantum simulations.

Future Plans: Complete the object-oriented C++ code for path integral Monte Carlo. Using this code, perform simulations of heavier elements such as energetic materials at high temperatures and pressures. Further develop and apply the Coupled-Electronic Ionic Monte Carlo to hot dense hydrogen, calculating the melting curve and the plasma phase transition. Extend this methodology to systems containing first row atoms. Novel methods for quickly obtaining trial functions are needed. Test newly-developed methods to calculate forces in molecular systems.

**Theoretical Advances in Understanding Nitrogen: Simulations at High Pressure and Temperature and Predictions of New Phases (Mattson and Martin)**

We have completed first-principles quantum molecular dynamics simulations of nitrogen at high pressures and temperatures, with the results presented in the thesis of W. D. Mattson and papers to be published. The work includes simulation of shock wave induced dissociation of N2 molecules, and a careful analysis of double shocks showing that shock induced cooling can occur in nitrogen. The most recent work during the last year has led to prediction of a new structure for nitrogen under high pressure, derived by simulations starting from the high pressure experimentally observed known structure for nitrogen. This new Hexagonally Packed Chain (HPC) structure consists of zig-zag chains packed in a simple hexagonal lattice and is metallic. Unlike other chain structures studied before, this one is
energetically competitive with the insulating, three-dimensional Cubic Gauche (CG) structure previously considered the most energetically favorable nitrogen structure above about 50 GPa. Molecular dynamics simulations show that both the HPC and CG structures are stable minima even at near ambient pressures. The existence of competing structures and the experimentally observed large barriers to phase transition (transitions are not observed below about 150 GPa) together imply that a metastable glassy like amorphous phase would be experimentally observable. In addition to the chain structure we found a structure that contained a mixture of both N₆ and N₂ molecules, which is higher energy but may be observable because energy barriers are lower for transitions to this structure.

The primary conclusions of our work are that under pressure nitrogen is predicted to exhibit a rich array of phases comparable to carbon. The existence of the metallic chain and insulating network structures of almost the same energy is analogous to graphite and diamond. Like carbon, condensed phases of nitrogen exhibit metastability. Unlike carbon, however, at low pressure nitrogen has molecular phases of much lower energy, and the metastable condensed phases are energetic materials with enormous energy per unit mass.