3.4 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

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

Rocfire is a tool currently being built to analyze the burning characteristics of heterogeneous solid propellants. The ultimate 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 three-dimensional simulation code, taking into account the gas phase, the solid phase, and the irregular regressing surface. Shown to the right are level surfaces of the total heat output in the gas phase. The

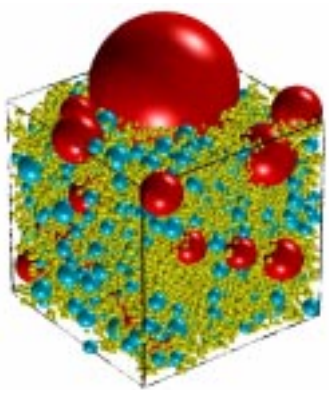

Fig. 3.4.1: *Rocpack* packing simulation for heterogeneous propellant. Realistic packing fraction (0.7698) achieved for 10000-particle simulation. Experimental volume fraction is 0.766.

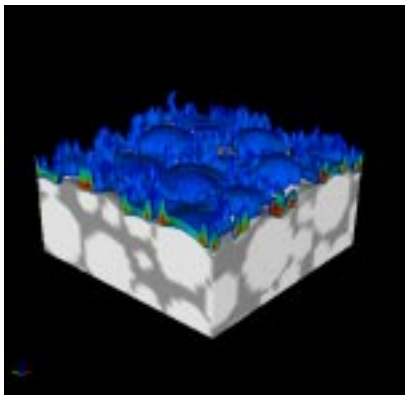

Fig. 3.4.2: *Rocfire* simulation of burning heterogeneous propellant. Flame colors represent total heat output in gas phase above corrugated surface—red is hottest, blue is coolest.

propellant morphology was computed using *Rocpack*, an in-house particle packing code. Rocketeer, an in-house visualization software package, generated the image.

Rocfire was recently parallelized using Fortran 90 and MPI. Figure 3.4.3 shows the results of scalability studies for *Rocfire* conducted on the ASCI Blue Pacific and on the CSE Turing cluster. The results are for a scaled problem (number of grid points increase with increasing number of processors) and for a fixed problem (20 million grid points).

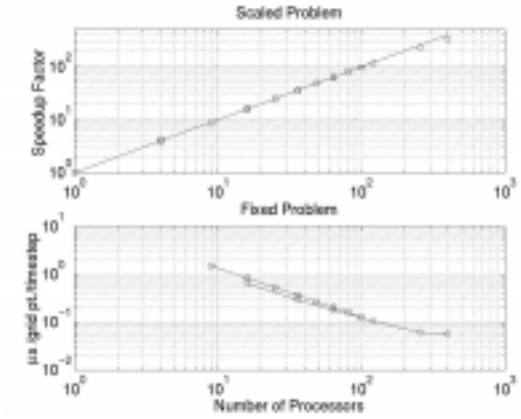

Fig. 3.4.3: Scalability studies for *Rocfire* conducted on ASCI Blue Pacific (circle) and on CSE Turing cluster (square).

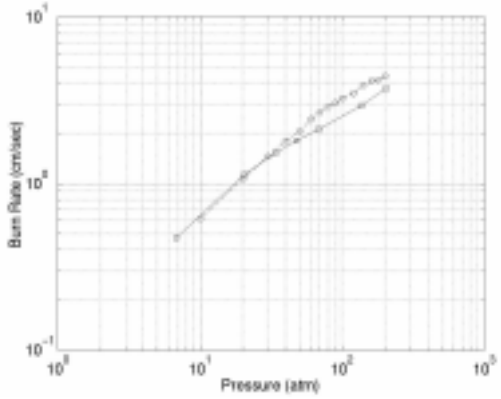

Fig. 3.4.4: *Rocfire* burn rate simulation results for Miller pack (top curve). Solid curve is Miller's experimental data.

For validation, burning rate simulations were carried out for Miller pack SD-III-17. Figure 3.4.4 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. Future work will focus on the further development and validation of *Rocfire*, relevant modeling and physics issues, and the development of an efficient algorithm for the implementation of a subgrid model into the CSAR system framework.

Dynamics of Flames in Rectangular Propellant Cracks (Short, Liu)

Thermal or shock ignition of a propellant can lead to fracture and cracking, which increases the available surface area of burning and may result in a dramatic change in the mode of combustion. We have been working towards an understanding of how burning takes place in a propellant crack and its implications for the safety and reliability of energetic materials.

Using direct numerical simulation of the zero Mach number Navier-Stokes equations, we have simulated flame behavior in the rectangular propellant crack geometry investigated experimentally by Berghout, Son and Asay carried out at the Los Alamos National Laboratory. Our calculations reveal that steady burning can exist provided the pressure inside the crack is sufficiently large for a given crack width or the crack sufficiently large for a given pressure. The flame is shown to oscillate up and down the crack under near-limit conditions, i.e., for a sufficiently small crack width and/or pressure, and sufficiently large Lewis numbers. These observations are entirely consistent with the experimental results and reveal oscillations in cracks can occur independently of the L* instability. Future plans include extension to more realistic crack geometries, including the effect of combustion driven crack propagation.

Modeling Thermomechanical Structure of Solid Propellant Flames (Stewart, Kuznetsov)

During the last year we have been analyzing the thermomechanical structure of solid propellant (SP) flames. This includes the temperature, velocity, stress and reaction profiles in both the solid and the gas, with an aim to carefully revisit traditional assumptions and models. We completed and published a simple, but thermodynamically consistent, model of a thermal expansion boundary layer that can occur near the melt or transition temperature in solid propellant constituents such as AP or HTPB. The results show the formation of a thin region near the edge of the solid surface where energy is consumed by thermal expansion work, which leads to a decrease in temperature and sharpening of the temperature gradient. The results also show a significant displacement or swelling of the material at the interface that may lead to material degradation and microcracking near the solid interface. This year we started work on extensions to multidimensional, time-dependent SP flame structures that are sensitive to the structure of the temperature profile.

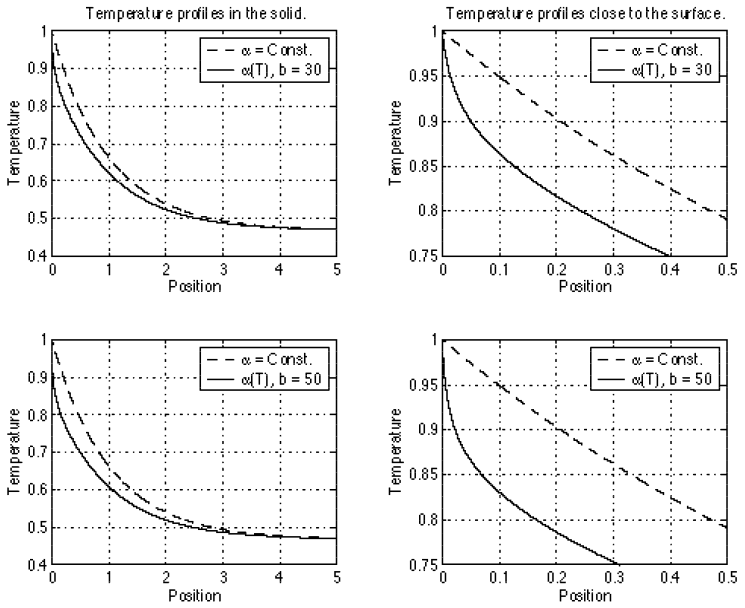

Fig. 3.4 5: Temperature profiles in AP computed for constant thermal expansion (dotted) and rapidly varying thermal expansion near the sublimation temperature (solid). All positions in microns.

Nonlinear Dynamic Burning Rate Simulation (Tang)

The phenomenological Zeldovich-Novozhilov nonlinear dynamic combustion model (*Rocburn*) has been successfully implemented in the integrated simulation codes (GEN1 and GEN 2). The coupled unsteady one-dimensional surface reaction condensed phase governing equations and quasi-steady empirical gas phase equations are solved numerically. The empirical gas phase expression reduces to the usual form for macroscopically steady burning conditions: $r_b = aP^n$. Nonlinear pressurization-rate dependent combustion during initial pressurization in solid propellant rockets is captured. To validate the dynamic combustion model for composite propellant, the "ignition" spike commonly ob-

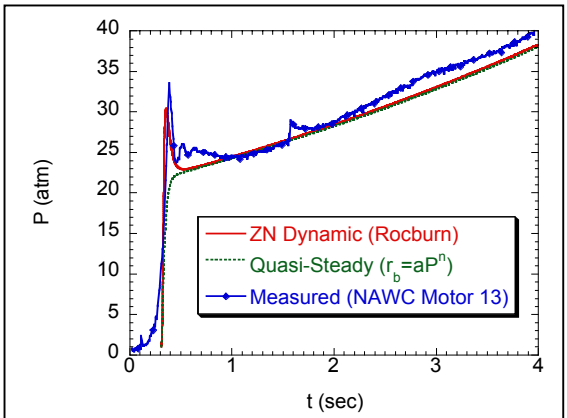

Fig. 3.4.6: Numerical and experimental NAWC tactical motor 13 pressure-time history (cylindrical grain, a=0.07696 cm/sec, n=0.461, P in atm, initial L* = 7.5 m).

served in motors with small L* (which is traditionally attributed to erosive burning or igniter mass flux) is simulated for a tactical motor with AP composite propellant, similar to what has been previously demonstrated for homogeneous propellant. Figure 3.4.6 shows the calculated and measured pressure-time history for NAWC motor 13 considering only bulk mode chamber filling and empting effect. No erosive burning has been included. There is also no structural coupling and no flowfield effects. The measured head-end pressure is compared with the numerical calculated pressure. The pressure spike behavior is reproduced well by the nonlinear dynamic combustion model (*Rocburn*) calculation without any particular adjustment of parameters and without considering the erosive burning effect. The quasi-static prediction (no dynamic burning) misses the spike entirely. Similarly, the result generated by the integrated system code (GEN1) that includes the three-dimensional flowfield effect draws the same conclusion.

Multi-dimensional Flame Structure and Propellant Regression Rate Simulation and Validation (Genevieve, Brewster)

The two-dimensional sandwich or laminate propellant configuration is being used to develop and validate simplified kinetics models for AP/hydrocarbon composite solid propellant combustion. The quantities being compared with experimental results to validate the model are gas-phase flame structure, burning surface profile, and regression rate. Our simulations include the effect of oxygenating the binder with fine-AP. This will allow us to simulate bimodal AP composite propellants that contain a bimodal size distribution of AP (coarse and fine).

Future efforts will be to validate the model based on comparison with experimental results, with the objective of achieving quantitative predictive capability. Specifically, efforts will be focussed on flames formed between AP laminae (representing coarse AP particles) and binder oxygenated with fine-AP particles. Another area of focus will be condensed-phase decomposition kinetics.

Structure of Burning Aluminum Particles in Solid Rocket Motors (Krier, Melcher)

The rate that aluminum particles burn and the structure of their oxide smoke clouds surrounding the aluminum droplets burning were studied in a solid rocket motor (SRM) flow. Chamber conditions were 6-22 atm and 2300 K, filled by burning a stoichiometric AP/HTPB propellant, with the burning aluminum droplets being generated by co-burning an aluminized solid propellant. Optical imaging of the burning droplets and surrounding smoke clouds

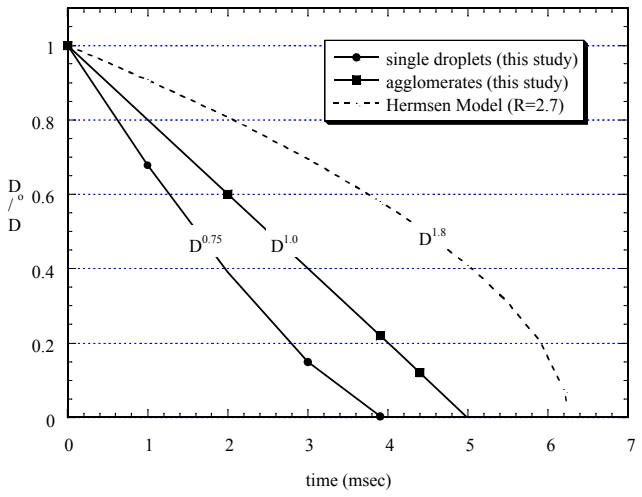

Fig. 3.4.7: Comparison of predicted mean burn history of 100 μm droplet for agglomerated droplet data, single droplet data, and Hermsen Model. For Hermsen model, rocket motor conditions at p = 15 atm and X_{eff} = 56%.

was conducted using a high-speed video CCD with high-magnification optics. An Abel inversion was used to de-convolute the imaged droplet intensity profiles to true intensity profiles. Measurements of the de-convoluted intensity profiles show that the non-dimensional smoke cloud size surrounding the burning droplets is not constant with diameter, but instead grows with smaller droplet diameters, by r/rs ~ D-0.5. A quasi one-dimensional model was also developed to describe the oxide cap accumulation on the droplet surface from the oxide smoke cloud surrounding the droplet. Modeling results suggest that less oxide accumulates in high-pressure SRM conditions when considering mass burning rates for different relative cap sizes. The final result of the correlation analysis, equation (a), is the corrected burning rate law for single droplets in SRM conditions (13-22 atm) for a 100 mm diameter single droplet:

$$D^a.75 = Do^a.75 - 8\ t \quad [mm, msec] \qquad (a)$$

Continuum Mechanics Strategies (Fried)

Research has continued on incorporating aspects of interfacial structure in a thermodynamically consistent and properly invariant model for a combustion layer as a sharp nonmaterial interface. An asymptotic analysis comparing the results of analogous one-dimensional problems formulated within a sharp-interface model for and a conventional combustion model has performed. This analysis yields forms for the constitutive equations in the sharp-interface model in terms of the well-recognized parameters of the conventional model. In addition, work has been performed on the foundation of the yield condition and flow rule in rate-independent finite-strain plasticity.

Simulation of Energetic Materials

Quantum Dynamics Methods (Martinez, Quenneville)

We are developing first-principles quantum dynamics methods (*ab initio* multiple spawning or "AIMS") and extending these to large molecules and condensed phases. In previous years, they have shown the feasibility of this approach for gas phase reactions of energetic molecules and also demonstrated the accuracy of the methods by direct comparison of simulations with experimental results for short time dynamics as probed by femtosecond spectroscopy. This year, we have probed the accuracy of the method for bond rupture processes of organic molecules important in combustion. We have also improved the treatment of electron correlation in AIMS, which can be an important factor in the accuracy of simulation results. A new fluctuating charge model has been proposed that will allow larger molecules to be treated. An AIMS study of the fluorescence quenching of excited OH radicals is in progress in order to better calibrate the rate of this reaction that is often used as a probe of OH radical concentration in combustion processes.

Over the coming year, we will focus on efficient implementation of some of the methods which have been tested at the conceptual level – time-displaced basis sets, quadratic valence bond fluctuating charge models, tunneling corrections in AIMS, and higher-order corrections for basis set propagation. We will also begin the application of AIMS methods to combustion reactions involving ammonium perchlorate and aluminum particles.

Path Integral Monte Carlo Simulations of Hot, Dense Hydrogen (Ceperley, Esler, Douchin)

We have further developed and tested better methods for Path Integral Monte Carlo simulations, and applied these new methods to dense hydrogen. We have continued study of the hydrogen phase-diagram and the nature of the transition from molecular hydrogen to metallic hydrogen. Good agreement has been shown at relatively low densities with semi-empirical theories and submitted for publication comparison of our calculations with double shock experiments. The results were presented at the international workshop on high-pressure physics at the Institute for Theoretical physics at UCSB. We have compared the efficiency of various quantum Monte Carlo methods to obtain the electron correlation energy and 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. In particular we performed simulations of molecular hydrogen in the temperature range of 1000K without assuming an intermolecular potential or a density functional for the electrons. The student supported by this grant (Esler) worked at LLNL as a visiting student during the summer 2001.

In the coming year we will continue work on hydrogen in conjunction with Berkhard Militzer at LLNL to produce a comprehensive equation of state and develop faster simulation methods; develop and apply a method for using pseudo-potentials in path integral Monte Carlo to allow simulations of heavier elements such as energetic materials at high temperatures and pressures; and further develop and apply the Coupled Electronic-Ionic Monte Carlo simulation technique.

Behavior of Molecular-scale Materials at High Temperatures and Pressures (Martin, Sanchez-Portal, Mattson)

During this year our work has come to an exciting point where we are making simulations to compare with new experiments that have uncovered a dense phase of nitrogen metastable at high pressure. Such phases have been predicted and indicated by shock wave data, but never before found at low temperature. CSAR investigators chose this problem because such a phase could be a model for energetic materials (essentially all energetic materials are nitrogen compounds); the recent experiments have given a new urgency and significance our simulations.

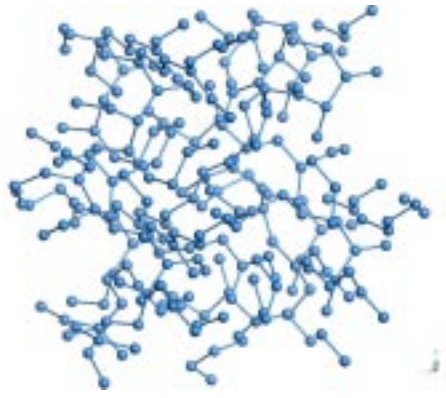

Fig. 3.4 8: Amorphous non-molecular connected network is formed when nitrogen is quenched at high pressure.

Our preliminary work has simulated shock waves in general agreement with the data of Nellis, et al., at LLNL, predicting molecular to non-molecular transformations at temperatures T~8000-12,000K. Upon quenching at high pressure (~200GPa) an amorphous non-molecular connected network is formed (Figure 3.4.8), which we find to be metastable at low temperature (<~300K) down to < 100 GPa in qualitative agreement with the recent experiments. This is an exciting result that opens new possibilities, e.g., adding other elements to stabilize energetic phases of nitrogen at atmospheric pressure.

In the future we will carry out more complete simulations of nitrogen and other molecular materials at high pressures and temperatures. The main issues will be to clarify the possible new structures for nitrogen at low temperature; to study reaction kinetics between different bonding states in the nitrogen system; and to proceed to hydrocarbons and systems containing C, N, H, and O. Reaction kinetics is the crucial issue both in the accuracy of the physical approximations and in the need for efficient algorithms to identify crucial, but rare, events in simulations.