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.

The Combustion and Energetic Materials (CEM) group has a hierarchical strategy for developing solid propellant combustion models based on incremental physical/modeling complexity and parallel experimental validation. Under this strategy the daunting complexity of composite solid propellant combustion is attacked by isolating various physical/chemical phenomena within a lowest dimensional model necessary to address each. Non-aluminized propellant issues are tackled first and then aluminum is added.

Under macroscopically steady conditions non-aluminized particulate propellant combustion modeling must address the following physical and chemical challenges:

1. Intrinsic unsteadiness due to particulate structure (3-D)
2. Multi-dimensional heat/mass transport and nonplanar burning surface (2-D)
3. Nonpremixed flame structure (2-D)
4. Interaction chemistry between fuel and oxidizer (2-D)
5. Premixed chemistry and flame structure (1-D)
6. Solid propellant thermal inertia (1-D)

Issue-(1) requires 3-D modeling with quasi-spherical oxidizer particles; (2-4) are best attacked in a 2-D configuration such as laminate propellants; (5-6) are best addressed with a 1-D model. Therefore our strategy is to isolate each phenomenon within the lowest dimensional model and validate at that level. This strategy allows the best chance for successfully modeling the most geometrically complex phenomenon (1) since uncertainty in the other issues is dealt with at an appropriate lower dimension. This strategy allows the development of confidence on the part of industrial and government scientists and engineers in the predictive capability of the models developed here by going beyond the usual high-level,

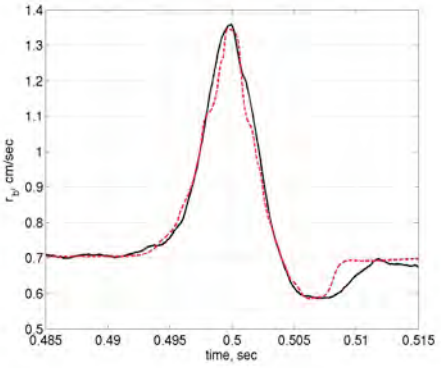

Fig. 3.2.1: Burn rate as function of time for pressure pulse. Results from *Rational_Rocburn* (red) compare well with multidimensional results from *Rocfire* (black).

steady burning-rate-only mode of validation. Our goal is to develop predictive capability and then demonstrate capability predictability through blind and double-blind testing. That is, we will propose motor firings and propellant combustion experiments and tests that have not been conducted yet and predict the results a priori.

Rocfire is a sub-grid model to address 2-D and 3-D issues (1-4). The *Rocburn* code was developed both to address 1-D subgrid modeling issues (5-6) and as the system code to run in a coupled, integrated mode. Gas-phase complexitites associated with issues (1-5) are homogenized into a look-up for gas-phase heat feedback to the propellant surface; the only phenomenon that is explicitly modeled in the system code *Rocburn* is (6). Currently *Rocfire* can simulate 2-D and 3-D nonaluminized propellant. Some features of aluminum such as particle emergence have been incorporated but agglomeration still needs to be added. Since aluminum burns in a very different mode than the non-metal ingredients (i.e., far from the burning surface) it requires quite different modeling treatment than oxidizer and binder. A model must be developed to simulate accumulation of the Al at the surface, agglomeration, ignition, and departure from the surface as agglomerates are swept away by hot product gases from the oxidizer and binder. Nevertheless there are several important issues, namely (2-4) that can now be addressed through validation by *Rocfire*. Experimental data on laminate propellants has now been obtained; and flame/surface structure regime map has been obtained.

There are two important types of macroscopically unsteady combustion that need to be modeled: pressure fluctuations (acoustic instability) and ignition transient (time-dependent heat flux). The latter involves an extrinsically imposed heat flux from hot igniter gases and particles including convective, conductive (particle impingement), and radiative heat transfer. A Monte Carlo model is being developed for photon absorption and scattering in the propellant. Propellant combustion response to external pressure fluctuations (i.e., response function) is being studied computationally. Validation of the propellant combustion response to pressure unsteadiness will require comparison with the extensive body of experimental data that is available in the literature.

Rocstar Module Development

Rocfire and *Rocburn* (Buckmaster, Jackson, Massa, and Wang)

We have developed what we call *Rational_Rocburn*, a *Rocburn* module that is constructed by spatial averaging of *Rocfire*, accounting for unsteady effects on the propellant time scale (Figure 3.2.1). A key component of this module is a look-up table that accounts for the heat flux to the propellant surface from the *Rocfire* combustion field. This module has been incorporated into *Rocstar* and a central goal of our group has now been achieved, albeit for non-aluminized propellants.

A variation of *Rocfire* (non-aluminized) has been developed using a 3-step kinetics model rather than a 2-step model as in the first implementation. Agreement with experimental burning rates of a group of propellant packs has been achieved. Further improvement in this respect is not expected. The new model leads to intrinsic instabilities under some circumstances, the stability boundaries of which are cannot not match reality, but there is no resolution of this difficulty within the framework of simplified, global kinetics.

Rocfire has been applied to an important physical problem, namely the burning response to an impinging

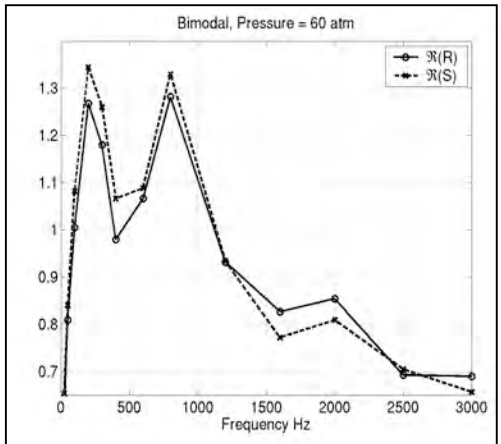

Fig. 3.2.2: Mass-flux response function (R) and velocity response function (S) as function of frequency for bimodal pack. Note response functions have multiple peaks.

acoustic wave. There are serious rocket stability issues should the reflected wave have a larger amplitude than the incident wave. We have been able to compare the mass-flux response function and the velocity response function (both functions of frequency) and have shown to what extent they differ (Figure 3.2.2). Since the velocity response can not be measure experimentally, whereas the mass-flux response can, it is always assumed that they are equal in making stability predictions, and we have described the errors that can arise in doing this.

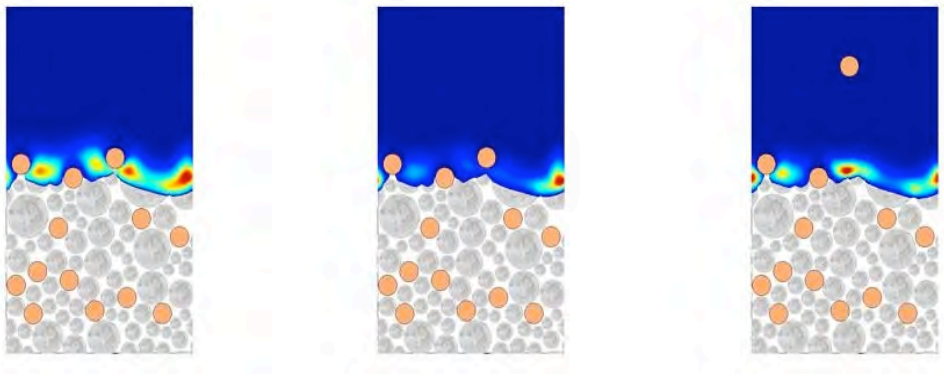

Fig. 3.2.3: Results from CSAR aluminum *Rocfire* code. Aluminum (shown in copper) is initially embedded within propellant. As propellant surface regresses due to burning, aluminum particle becomes exposed to hot gases, detaches, and then moves away from surface. Surface regression, detachment and subsequent evolution of aluminum particles, are handled using level sets.

The integration of *Rational_Rocburn* into *Rocstar* has recently been completed, and attempts will be made to develop a similar module for aluminized propellants.

Work on aluminized *Rocfire* will continue (Figure 3.2.3) toward a 3-D version. We believe that the most important contribution that can be made here is to the agglomeration problem, one of enormous interest to the US industry and of at least equal value to any *Rocstar* application (Figure 3.2.4). We are also examining the role of Alex (micron-scale aluminum) in the combustion process, as there is considerable interest in this in the industry. The aluminum work and related issues (such as melt layers) could easily extend to the end of the current contract period, but we expect that interim results within the two-year framework will be of fundamental value to the integrated code. The role of non-spherical AP particles on the burning characteristics is presently being examined, and we expect to provide a detailed description of these effects within the next year.

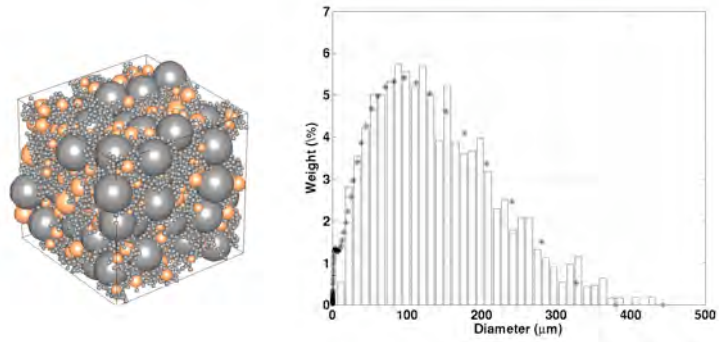

Fig. 3.2.4: Left — three-dimensional propellant generated from CSAR packing code, *Rocpack*. AP particles shown in gray, aluminum particles shown in copper. Right — agglomeration model results comparing agglomeration distribution from experiments (symbols) with our model (histogram). Agreement between our model and experiments is very good.

The far-field of *Rocfire* (~ 1mm from the surface) is being examined for very large packs in an attempt to characterize the flow field fluctuations that should be used as boundary conditions for the LES simulations of the Fluids Group. We have already found that 2-D results are not of interest, as

they differ significantly from the 3-D results, but we expect to characterize the 3-D field within the next year.

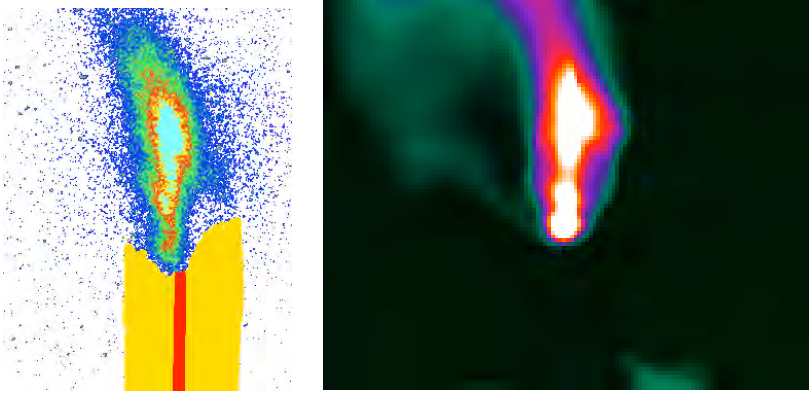

Fig. 3.2.5: Simultaneous UV (left) and IR (right) images of IPDI-cured pure binder (160 μm thick) laminate AP/HTPB propellant at 17.9 atm

Flame Structure, Regression Rate, and Propellant Ignition Validation (Brewster, Fitzgerald, Cain, and Tang)

The laminate propellant configuration is being used to develop and validate kinetics and other modeling assumptions for AP/hydrocarbon composite solid propellant combustion. In particular an effort is being made to improve the reliability for predicting combustion of oxygenated binder and to do extensive comparison between simulation predictions and experimental observations. To this end a regime map of flame/burning surface structure (split, nonpremixed versus merged, diffusion flame structure) has been generated and reported. It now remains to detailed comparison with models whose purpose is to simulate heterogeneous solid propellant combustion, such as *Rocfire*. In addition, flame structure is also being investigated through IR emission imaging.

The IR images shown in Figure 3.2.5 represent preliminary results obtained using the method of simultaneous UV and IR emission imaging. Because the IR image capture rate is greater than for previous UV imaging, time-dependent features are being resolved better, such as in the flame structure. The IR images indicate a feature not seen in the UV images, namely two distinct regions of emission, one near the surface and one farther away. Ultimately the scientific goal (in addition to the programmatic goal of developing and validation an AP/HC combustion model) is to provide an explanation for the unique capability of AP to form strong diffusion flames.

Chemical kinetics are being investigated to develop mechanisms kinetic parameters that are consistent with the observed UV and IR flame structures as well as surface topological structure. IR imaging spectroscopy is also being developed to give evidence of the state of the emitting species, which will help corroborate the postulated mechanisms. All of this data for flame and surface structure can and should be used to validate the kinetics and other modeling assumptions in *Rocfire*.

Simulation and experimental validation of radiant ignition of an AP-composite propellant similar to RSRM Space Shuttle propellant but with variable optical properties is being carried out. The simulation uses a surface temperature ignition model. The experimental validation used a CO_2 laser and AP-composite propellant with various amounts of carbon black added to vary the absorption coefficient or opacity. 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 for ignition threshold. The ignition time decreases as laser flux increases. At lower fluxes increasing the opacity decreases ignition time whereas at higher fluxes this effect appears to go away and possibly reverses. These effects need to be investigated computationally.

The experimental results so far have shown that (i) in-depth absorption and scattering are important, (ii) that the ignition process is still highly localized and three-dimensional and (iii) that selective ignition temperature criteria are needed to be able to accurately describe mixed radiative and convective heating and ignition. Accordingly a new effort was begun 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.

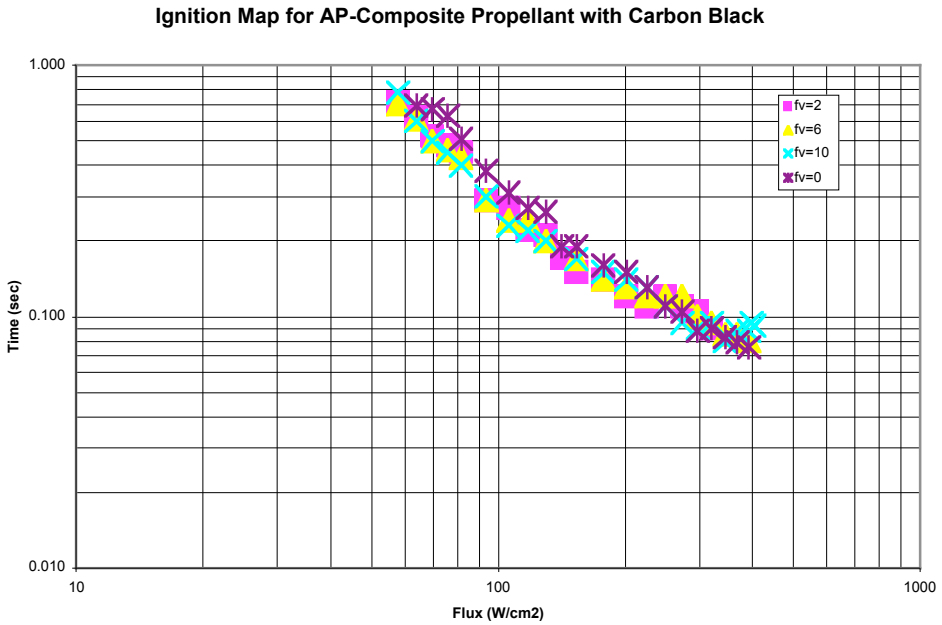

Fig. 3.2.6: Go/No-Go ignition map for AP-composite propellant at 1 atm using CO_2 laser. Absorption coefficient is varied by varying carbon black volume fraction (fv).

Combustion Validation Projects

Stable Quasi-Steady Motor Burning (Stewart, Brewster, Tang, Yoo, Kuznetsov, and Willcox)

An important issue in front of CSAR is computability of long-time solutions for rocket burn. Marching at the CFL prescribed time step is not viable for practical computation; another strategy is required. Using rigorous asymptotic analyses, it was shown that rocket motor burnout can be viewed as a quasi-steady process and reduced equations have been derived for accelerated time integration strategies. At each reduced time step a steady transonic flow must be calculated and methods developed problems in aerospace industry for computational aerodynamics can be used.

An industry standard, quasi-one dimensional rocket motor model proposed by Mark Salita has been implemented to serve as the basis for testing and

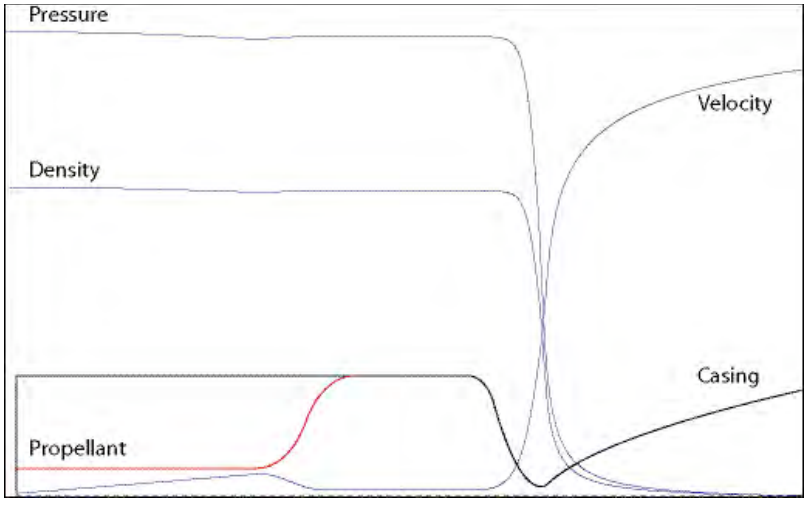

Fig. 3.2.7: Steady state profiles of state variables

validation of the stable quasi-steady burning in *Rocstar*. Our validation code incorporates a high-resolution Euler solver (*AXS*) and a high order, level-set surface evolver (*WaveTracker*) to compute a modified Euler equations rocket model in a geometry that is close to real motor design and can be later transferred directly to *Rocflo* for testing. Exact one-dimensional solutions were developed to validate the approach, determine accuracy and convergence and measure relaxation times to a steady state in fixed geometry given a core configuration change. A typical steady injection profile is shown in (Figure 3.2.7).

The combined *WaveTracker/ODE* (steady injection flow) solver was used to perform complete motor burnout tests (Figure 3.2.8) to estimate an upper bound speed up of the total simulation. As an example, for 200 points, the CFL condition imposed by *WaveTracker* requires 5000 iterations for a complete burn-out of 140 seconds (dt=0.02), while Euler solver time step for the same resolution would be dt=0.000007, requiring 20,000,000 iterations. Therefore, an upper bound speedup estimate is 4,000 times. Multi-grid is being implemented to replace the ODE solver and to test more general methods of determining quasi-steady flow configurations for accelerated long-time stable burn marching in 2-D axisymmetric and 3-D flow.

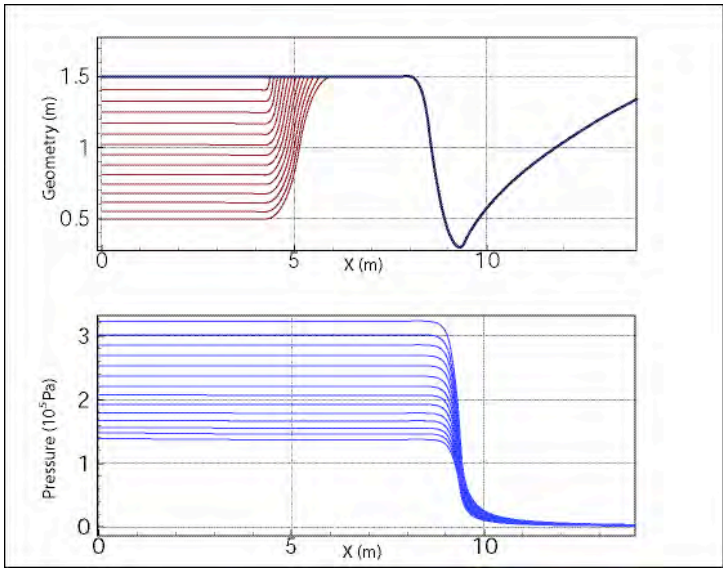

Fig. 3.2.8 Burnout test of 140 seconds.

A 3D MATLAB code was developed to generate a zero level set input file for the *WaveTracker* using an output from a rocket geometry model designed in Pro-E. Our efforts will enable us to run test configurations in both the AXS/WT code and *Rocflo* through transfer to Gridgen. As a result we now have the framework for a rocket design and simulation tool based on simplified physics that can fill in the gaps where *Rocstar* can not run the full time-history of the motor due to computer time limitations. This framework is illustrated in Figure 3.2.9.

Thermo-Mechanical and Curvature Effects in SP Deflagration (Stewart and Kuznetsov)

Continuing our effort to model curvilinear deflagration of energetic material with thermal expansion, we focused on building simulation tools that allow us to verify obtained theoretical results, and to study combined effects of expansion and curvature on the burning of solid propellant particles. We developed a one-dimensional code for unsteady burning of a spherical particle, which apart from being a test bed for our theory, turns out to be an interesting supplement to a widely studied classical problem of decomposition of a spherical monopropellant droplet in the inert atmosphere.

Extensive study of computational models was performed last year in order to choose appropriate numerical tools. Interface-tracking algorithms for interfaces that travel across a fixed grid were ruled out as lacking accuracy. In the case when high activation energy of the solid phase reaction makes deflagration process extremely sensitive, wild fluctuations of the burning surface temperature occur. A fixed surface algorithm, which is more stable and accurate choice for spherical symmetry, is used instead. Parametric study of the particle burning is under way. We observe that unlike classical gas-

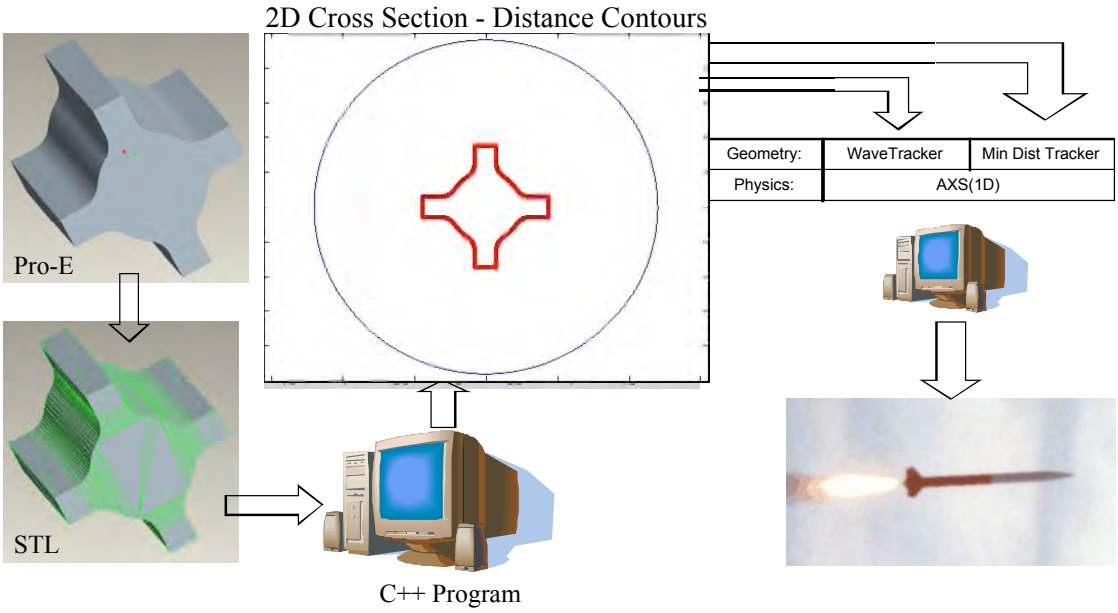

Fig. 3.2.9: Solid rocket design and simulation tool using minimum distance function to represent propellant grain geometry and simplified physics modules to accomplish long-time-scale simulation within *Rocstar*

phase controlled particle deflagration, where Damkohler number solely defines burn rate, we find that both the Damkohler number and curvature define it (Figure 3.2.10). Also, we are looking at the limit of small particles; with radii comparable to the preheat zone thickness, where multiple solution branches for the regression rate as function of Damkohler number are observed (Figure 3.2.11). Results of this parametric study will be presented in a paper. The next step will be to study combined effects of curvature and thermal expansion, which we plan for the Fall 2004.

The project plan is to continue work on developing multi-scale theory and numerical tests cases that can be used to validate of rocket flows generated by *Rocstar*. The work will be focused on application to accelerated long-term burn simulations for 2-D axisymmetric and full 3-D solid rocket motor flows. Theoretical work will continue to develop rationally derived asymptotic models for reduced flows that can be used by *Rocstar*, that are resolved on the longer time scales of the motion of the regressing solid propellant interface. So far rigorous asymptotic analyses has developed reduced equations for time integration on the surface regression time scale, as opposed to the acoustic time scale. Exact 1-D (steady injection) profiles have been developed. It was estimated so far that theoretical speed ups of O(1000) are possible by solving the reduced equations. We will

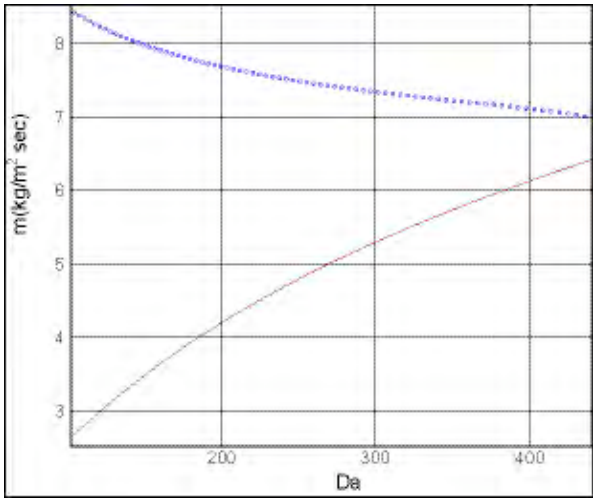

Fig. 3.2.10: Results of two experiments of burning 0.001 m diameter HMX particle with varying Damkohler number, which is proportional to product of particle radius and ambient pressure squared, by decreasing ambient pressure from 20atm and keeping radius of particle constant (blue curve), and by decreasing radius of particle and keeping pressure con-

take into account additional complexities not yet addressed of large recirculation regions, in 2-D and 3-D, and other physics. This may include modified wall boundary conditions that come from averaging theories as suggested by Moser.

We will also continue to develop a numerical testing basis for rocket flows that can be used for validations of *Rocstar* and provide rapid verifications of different time integration strategies that will arise. Currently our work has been to develop solutions to the quasi-one dimensional Euler rocket model of Salita, coupled to a surface regression solver. Our validation code incorporates a high-resolution Euler solver (*AXS*) and a high order, level-set surface evolver (Wave Tracker) to compute a modified Euler equations rocket model in a geometry that is close to real motor design and can be later transferred directly to *Rocflo* for testing via compatibility with Gridgen.

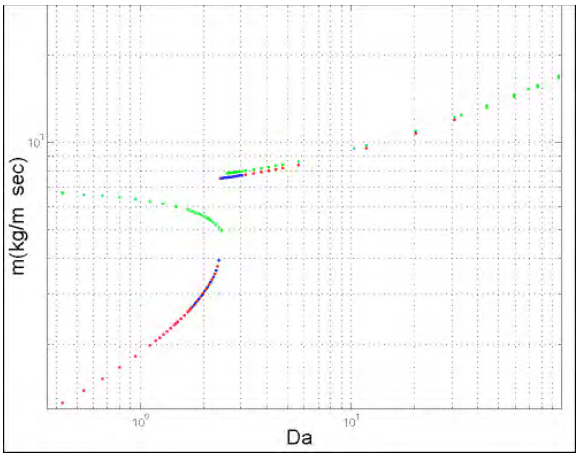

Fig. 3.2.11: Quasi-steady calculation of mass flux for small Damkohler numbers

Combustion Studies

Combustion in Propellant Cracks (Short, Kessler, Geubelle, Breitenfeld, Haselbacher, Massa, Roe)

We have been using a reaction modified form of Rocstar to investigate the structure, dynamics, and instabilities of burning inside narrow propellant cracks. This group is interacting with a group at Los Alamos National Laboratory who has an on-going experimental program in propellant crack combustion. The focus of the simulations is to provide insights and predictions on issues such as critical crack width and chamber pressure that will support combustion, physical mechanisms of combustion instabilities observed in experiments, and combustion driven crack propagation. The *Rocstar* module has been modified to include some basic exothermic chemistry in the gas phase, and validation and verification conducted on basic combustion problems, such as reproducing the dynamics of planar strained flames in counterflows.

Short and Kessler have also been working towards providing validation and verification tools and results for the Rocstar simulation of burning in propellant cracks. Specifically, some original analytical solutions to compressible flow in long thin channels with surface regression are being developed. Kessler has also developed a very high order numerical solver specifically for the crack combustion problem that should accurately capture the acoustic/viscous/chemistry interactions on-going in the crack, so that the accuracy and performance of the *Rocstar* module can be evaluated.

The project plans of Short and Kessler involves two investigations. We will continue to use *Rocstar* to investigate the dynamics of combustion in propellant cracks. This is an important problem for issues such as stable rocket motor performance, but also one that is important for the DOE in understanding high energetic material performance under damage. Recently, colleagues at LANL have been conducting new experiments in this area, in different geometries where new physics play an important role. The intention will be to use *Rocstar* to model these new experiments. We also continue to develop validation and verification tools for the reaction modified *Rocstar* module. Along these lines, Kessler is going to study more effective ways of including chemistry source terms in the Rocstar module than the current split methodology.

Kessler will also use *Rocstar* to examine 3-D combustion in a microburner/fuel cell application, a problem which turns out to be highly related to the combustion crack issue, and would require little modification of the reaction modified *Rocstar* module. Micro-fuel-cell problems are of much current interest for developing portable energy supplies, and this will be an ideal problem to use *Rocstar* to simulate.

Aluminum Particle Combustion (Krier and Aita)

Ultrafine aluminum particles (e.g., Alex) are being used in more applications and knowledge of the difference between the ultrafine and larger combustion phenomena is important. For example, the burning rate dependence must have a transition from being diffusion dependent to kinetic dependent at a finite value for the particle size. A new model is being formulated that will extend the current model to include Aluminum particles with size ranging from 2–50 μm. Because of the small diameter particles, this combustion regime is more heavily transient dependent. The model is based on a shrinking core formulation with constant outer diameter. The inner core consists of aluminum while the outer shell consists of the aluminum oxide. The oxidation of the inner core is dependent on the diffusion of oxidant from the surface. The model also includes the conservation equations of mass, species, energy, and momentum. The boiling temperature of Alumina is an important input parameter in the currently excepted Aluminum combustion model. A current literature search results in three studies in which the boiling temperature of Alumina (Al_2O_3) was determined experimentally. The earliest results provide a boiling temperature of 3250 K while later results indicate a boiling temperature for Alumina of 3750 – 3800 K at atmospheric pressure. This differs from the currently used temperature of ~4000 K which leads us to wonder what value is appropriate to use. The boiling temperature of Alumina will be inspected experimentally in a shock tube. The temperature and pressure can be varied in the shock tube while the amount of light scattering can be measured. This data will be used to find the boiling temperature of Alumina and the pressure dependent relationship. The predictions of the model will be validated using shock tube experimental data of small aluminum particles. The experimental data provides burn times that can be compared directly to the model. The validated model will then be used along with different sized aluminum particles to determine the range of accuracy. The current model also assumes an oxide lobe upon ignition. There is a transient step in which the oxide covering the particle coalescences into a lobe. While the assumption of an oxide lobe may be accurate for larger particles, for which the oxide shell has time to coalesce into a lobe, the current focus is on a model that will cover smaller particle diameters. The model formulated along with the current model will be used to inspect the range of particle sizes in which the Glassman criterion and the diffusion/kinetic limit assumption can be used. The conditions for transition between models will be determined experimentally. The d^n law will also be inspected to ascertain the value of n and its dependence on various parameters. The value of n will also be compared to previous experimental work done by Melcher, Burton, and Krier (*JPP,*2002). The model predictions will be used to study current problems associated with the module *Rocfire*. These problems are:

- Ignition time and height of single aluminum particle in fine AP
- Time resolved temperature history of Aluminum convected off propellant surface
- Inspect Cohen's melt temperature criteria
- Burn rate of propellant vs. pressure for different amount (%) of Alex

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 including novel forms for the wavefunction and methods for sampling electronic configurations more efficiently. 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.

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 proton zero-point motion and found values for the melting temperature of solid hydrogen at high pressures. We have developed and tested a new method to compute forces using quantum Monte Carlo and made the first such calculations on polyatomic molecules with higher accuracy than with any other method. We have developed a new method and codes to eliminate core electrons and have tested these pseudopotentials on several atoms and moleculaes. We have completed a new object oriented code in C++ to perform Path Integral Monte Carlo using these pseudopotentials.

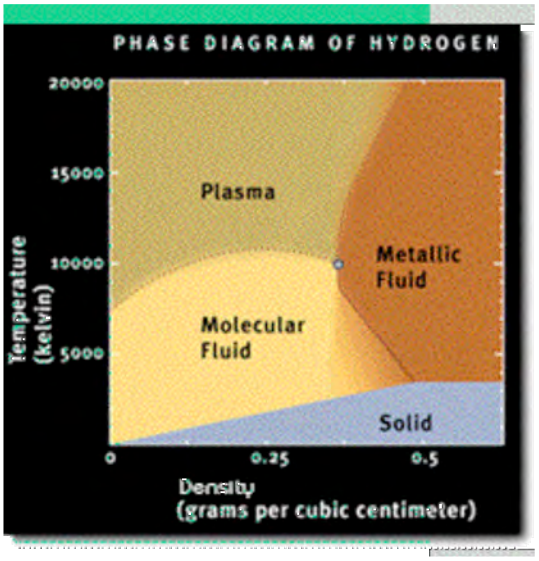

Fig. 3.2.12: Four different phase of warm dense hydrogen. Newly-developed CEIMC method has allowed calculations down to room temperature, much lower than previously and with much more accuracy.