

## 3.4 Combustion and Energetic Materials

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### Overview

Combustion of solid propellant composed of energetic materials is the driving thermo-mechanical 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.

### Combustion Interface

The combustion region at the interface between the chamber flow and the propellant is thin, on the order of tens of microns. In contrast, the overall dimensions of the RSRM are measured in meters. Hence, the integrated system code must treat the combustion layer as an interface across which mass, momentum, and energy are given in terms of jump conditions. There are a number of strategies of varying sophistication with which to generate these conditions. The most detailed approach is the generation of a complete sub-grid combustion model (called *Rocfire*), a three-dimensional unsteady simulation of the propellant flames, the thermal layer in the solid, and the unsteady nonuniform regression of the solid surface. This work is being carried out under the leadership of Buckmaster and Jackson. Three significant milestones have been achieved in Y3 in this area: a packing model for heterogeneous propellants has been developed; *Rocfire* has been implemented in the context of sandwich propellants;

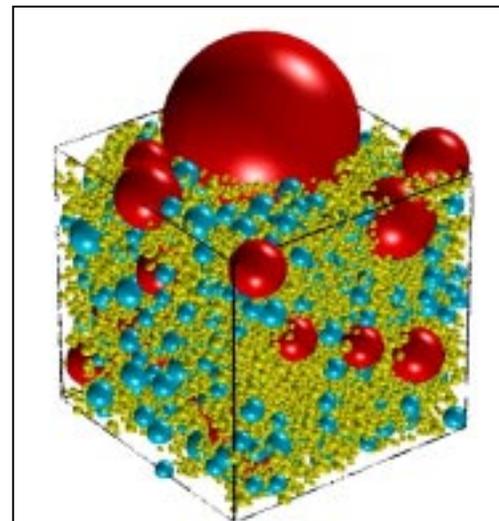


Fig. 3.4.1: Packing simulation for heterogeneous propellant. Realistic packing fraction (0.7698) achieved for 10000 particle simulation. Experimental volume fraction is 0.766.

and *Rocfire* has been implemented in the context of a two-dimensional randomly packed propellant.

Typical solid rocket motor propellants, such as those used in the RSRM, are composed of particles of ammonium perchlorate (AP) and aluminum (Al) embedded in a fuel binder. Since the burning rate of a heterogeneous propellant is influenced by the propellant morphology and by the size and size-distribution of AP particles, a method for generating model morphologies is required. A strategy for doing this—a random packing algorithm—has been developed in collaboration with Knott. It is a seminal contribution to propellant studies. The models generated in this way consist of random distributions of varying size spheres in a periodic cube (Figure 3.4.1).

The packing fractions (volume percent of AP) generated by the algorithm have been successfully compared with existing experimental data for bimodal packs. In addition, industrial AP data (obtained from R. Bennett of Thiokol Corporation) has been used by Kochevets to define realistic packs with packing fractions that closely approximate those of true propellants. Future work includes modifying the algorithm to run on parallel platforms (necessary to generate packs with 100,000 or more particles), testing the code against an extensive experimental database, determining the overall statistics of the various packs, and identifying pack-defined length and time scales that might interact with rocket chamber gas flow processes.

Random propellant packs generated by the packing algorithm can support a complex three-dimensional combustion field that is coupled to thermal processes in the solid. *Rocfire* is concerned with the detailed simulation of this field, and a preliminary version of *Rocfire* has been generated in collaboration with Hegab. The code describes the unsteady burning of a heterogeneous propellant by simultaneously solving the combustion field in the gas-phase and the thermal field in the solid-phase, with appropriate jump conditions across the gas/solid interface. The model accounts for propagation of the nonuniform surface, the AP decomposition flame, reaction between the AP products and the binder gases, different material properties of the AP and binder, temperature-dependent gas-phase transport properties, and a full accounting of the equations of motion. No calculations of this kind have been described before in the literature.

A periodic sandwich propellant consisting of alternating slices of AP and binder has been used as a platform for developing the model and for the exploration of basic propellant-burning physics. Figure 3.4.2 shows the retreating surface at various times, and the flames responsible for this regression. Following initial transients, the

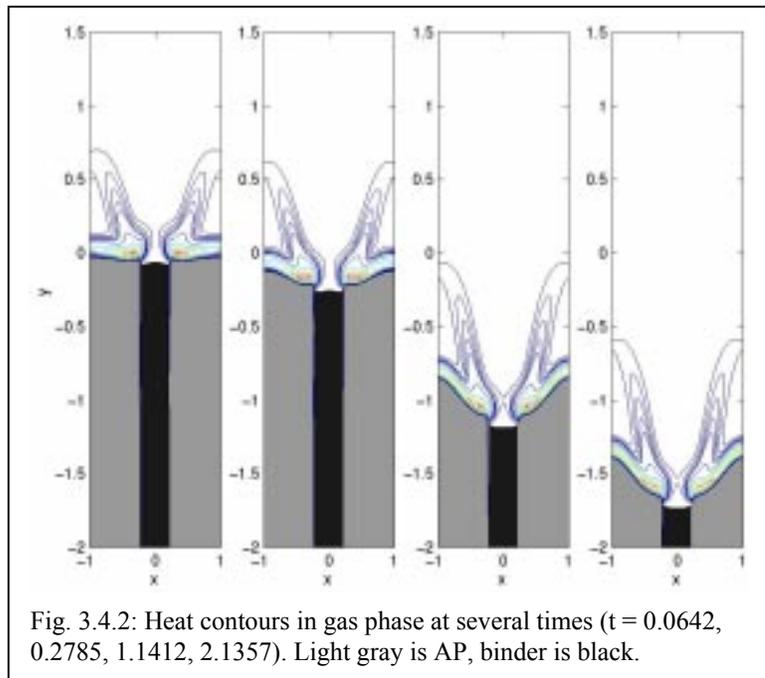


Fig. 3.4.2: Heat contours in gas phase at several times ( $t = 0.0642, 0.2785, 1.1412, 2.1357$ ). Light gray is AP, binder is black.

regression is steady, with unchanging shape. Calculations of this nature have enabled us to explore the effects of pressure, stoichiometry, sandwich thickness, and other parameters on the overall burning rate.

Non-periodic sandwich propellants have been studied in the laboratory, but rocket flames need to be examined in the context of random particle packings. The first implementation of *ROCFIRE* in this context is for two-dimensional packs where the AP particles are treated as disks, so that the combustion field is two-dimensional. This work is being done in collaboration with Hegab and M. Ulrich (AAE graduate student), and is also seminal in nature. Results of a typical calculation are shown in Figure 3.4.3, where the reaction rate and fuel contours are plotted at an instant of time. These calculations permit the prediction of morphology-induced fluctuations in the burning rate, the effects of the AP size distribution on the average burning rate, the response of the burning rate to chamber pressure disturbances, etc. In the future this will be done in a three-dimensional context for which ASCI level resources will be needed. More information about *Rocfire*, including several movies, can be found at <http://csar.uiuc.edu/~tlj/rocfire.html>.

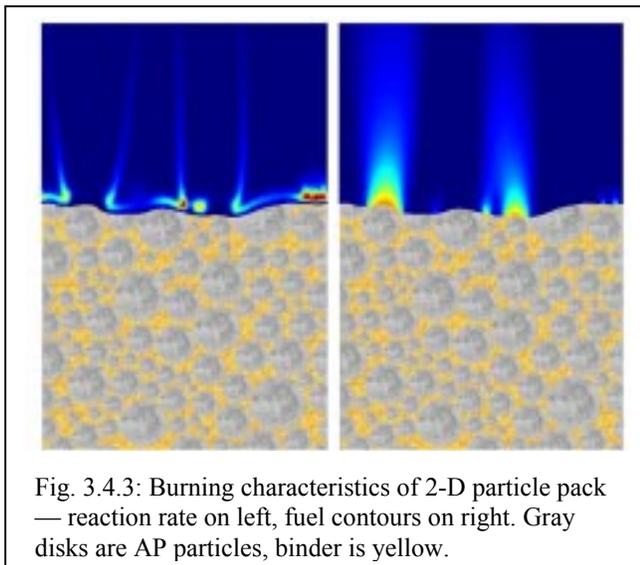


Fig. 3.4.3: Burning characteristics of 2-D particle pack — reaction rate on left, fuel contours on right. Gray disks are AP particles, binder is yellow.

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## Homogenization

Brewster and Tang are examining a simpler strategy for dealing with the combustion interface between the chamber gas flow and the bulk solid, one that essentially corresponds to a homogenization of the *Rocfire* picture. Both the combustion field and the thermal field in the solid are described by one-dimensional physics. The result is a relatively simple formulation for the interface jump conditions that preserves some of the important physics and can provide a useful interim interface description while *Rocfire* is further developed. On slow time scales the description is a steady one, and yields the familiar  $c = Ap^n$  formula relating the regression rate,  $c$ , to the pressure. But at shorter time scales the transient storage of energy in the solid is accounted for by numerical solution of the one-dimensional unsteady heat conduction equation, and then the response of the burning rate to transients is richer. This model has been used to study the combustion-fluid coupling in a simplified composite propellant  $L^*$  combustor, and shows that the difference between an unsteady description and the quasi-steady description can be significant when the pressure changes rapidly with time.

Figure 3.4.4 compares tactical motor pressure histories employing this model. The unsteady burning rate is significantly larger than the quasi-steady burning rate during the initial pressurization stage of the burn; the unsteady burning rate model is able to simulate the observed initial pressure, while the quasi-steady burning rate model fails to do so. The results suggest that, contrary to conjecture in the literature, the rapid rate of initial pressurization and

the “ignition” spike are not due to erosive burning or other complicated fluid and flame dynamical effects.

The dynamic regression rate model development, validation, and integration will continue, with the first priority being implementation of a new model (*Rocburn*) into the integrated simulation codes (*Rocface*, *Rocflo*, and *Rocsolid*).

Model development and validation will also continue with emphasis on validation for composite propellant combustion. Refinement of the empirically-based gas phase model to better represent the composite propellant combustion behavior is being conducted. Dynamic burning conditions, such as beginning and ending transients and unsteady oscillatory burning, will be investigated.

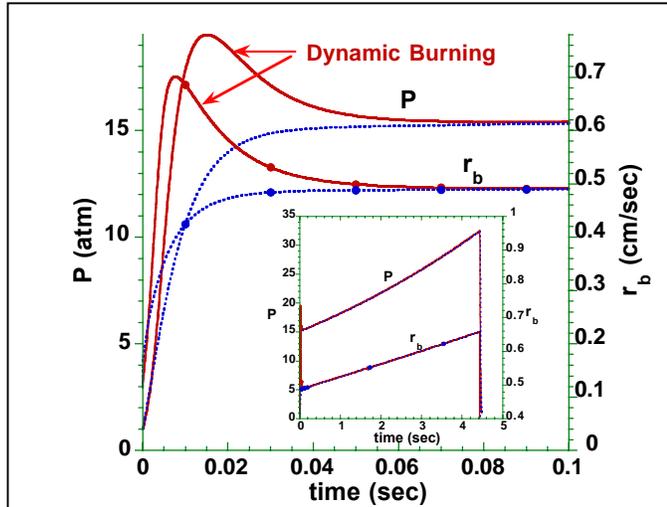


Fig. 3.4.4: Comparison of tactical motor pressure history predictions between unsteady burning rate model and quasi-steady state burning rate model (cylindrical grain,  $a=0.168$  cm/sec,  $n=0.392$ , initial  $L^* = 2.4$  m).

Fried and Short are adopting a third strategy for assessing the jump conditions across the combustion interface, one that does not make assumptions about the interface structure but rather uses the tools of modern continuum mechanics to develop thermodynamically consistent conditions and constitutive relationships. Their research has focused on incorporating aspects of interfacial structure in a thermodynamically consistent and properly invariant model for a combustion layer as a sharp nonmaterial interface. This model includes three additional interface conditions. These conditions determine the interfacial energy release, the interfacial friction, and the interfacial heating constitutively as functions of the interfacial mass flux, the interfacial velocity slip, and the interfacial temperature jump. As such, they embody the microphysical mechanisms associated with the change of phase and chemistry that occurs across the interface. In the simplest situation, when the interfacial free-energy density is constant, the relation determining the interfacial energy release contains a term associated with surface tension. This relation yields an evolution equation that is directly analogous to those arising in asymptotic models. Another feature of this theory is that it accounts for the transient addition of mass to the combustion layer.

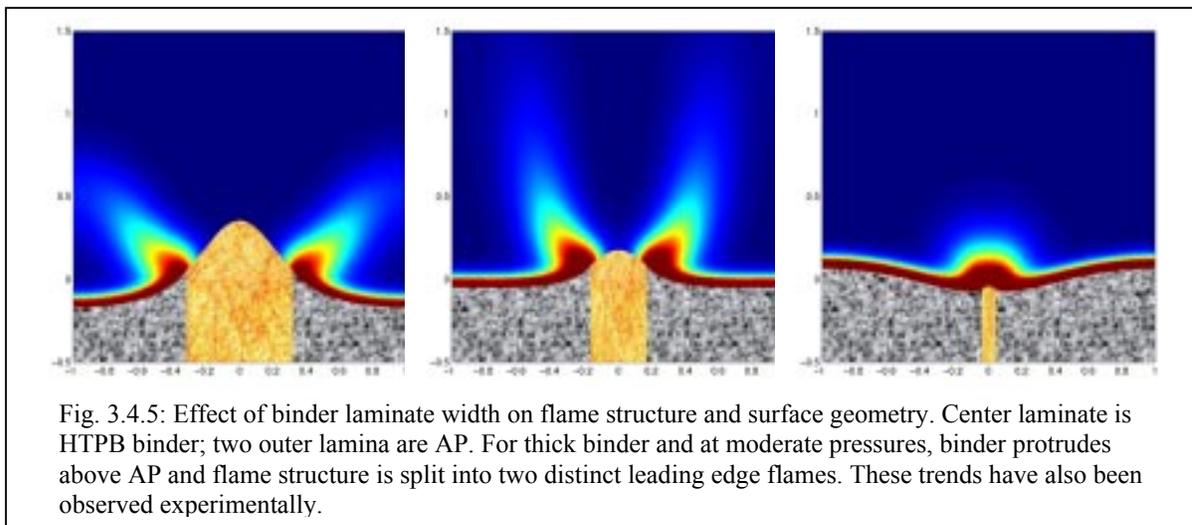
In the future the research will focus on obtaining a correspondence between the supplemental interface equations that arise in this generalized theory and the interfacial evolution equations that are used conventionally by scientists in the combustion community. An effort will be made to develop numerical methods for the solution of simple problems suggested by the theory.

## Flame Modeling Efforts

In addition to the *Rocfire* efforts, Brewster and Knott have carried out propellant flame calculations. Their model considers the steady regression (late time behavior) of a periodic sandwich propellant with full coupling between the two phases. The gas flow is described

using an Oseen approximation, one that has been validated by *Rocfire* for this configuration when the propellant surface slope is modest.

This model is being used to develop and validate simplified kinetics simulations. The macroscopic metrics being compared with experimental results to this end are gas-phase flame structure, burning surface profile, and regression rate. As an example, Figure 3.4.5 shows that the model correctly predicts that, for thick binders and moderate pressures, the flame structure is split and displays two leading edge flames separated by the binder that protrudes above the AP surface. Trends matching experimental observations are also predicted when the binder thickness and pressure are varied. A singular strength of this effort is



that experimental data on sandwich propellant burning is available from Brewster's laboratory studies supported by CNEM. Future efforts will focus on continuing the model development for AP with pure binder with emphasis on experimental validation. Various simplified kinetics schemes will be examined as will the effect of oxygenating the binder with fine-AP.

An independent flame-modeling effort is also being carried out by Krier and Surzhikov. Coupling between the two phases is accounted for and the Navier-Stokes equations are included in the description of the gas phase, but the propellant surface is assumed to remain flat. The AP oxidizer and the binder are stacked in regular, alternating bundles of a prescribed width and thickness. A complex kinetic model that accounts for eight distinct species notably characterizes the ongoing work.

*Rocfire* presently uses a finite Mach number code. Short and Liu have developed a three-dimensional, variable density, zero Mach number code suitable for the examination of both steady and unsteady propellant behavior on arbitrary geometries. This is presently being integrated into *Rocfire*. The routine uses a predictor-corrector scheme and Chorin's projection method. Currently they are developing a structured adaptive mesh refinement routine that will permit high-resolution calculations with multi-step complex chemistry (Figure 3.4.6).

The code is presently being used to study two model problems, unsteady propellant ignition and flame structure in propellant cracks. The first is concerned with how the ignition of heterogeneous propellants occurs

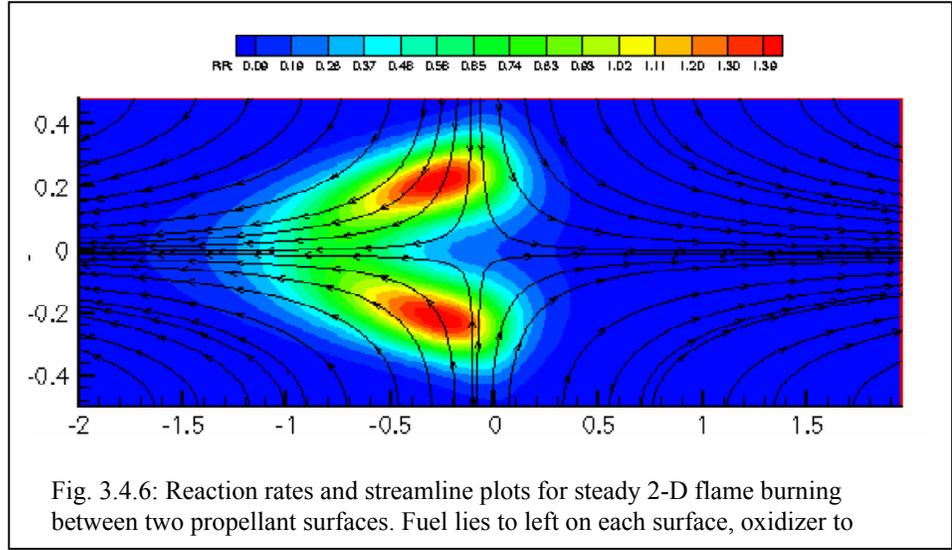


Fig. 3.4.6: Reaction rates and streamline plots for steady 2-D flame burning between two propellant surfaces. Fuel lies to left on each surface, oxidizer to

and whether certain configurations are easier to ignite than others. The second looks at flame structure between two propellant surfaces and examines how burning rates are affected by burning in a crack rather than at an unconfined propellant surface.

## Thermal Expansion of Propellant

Kouznetsov and Stewart have been assessing the role of thermal expansion in the solid during combustion and have discovered how the thermal expansion affects both the thermal and stress profiles in the solid as it undergoes an increase in temperature near the surface. They have used a three-dimensional, thermodynamically consistent formulation of the conservation laws for a thermoelastic solid, and have constructed an analytical solution for steady planar regression of the propellant surface, including a description of the thermal profile in the solid. They have shown that thermal expansion insulates the burning surface and can significantly reduce the mean temperature in a thin region within the thermal boundary layer where energy is consumed by expansion. This sharpens the temperature gradient at the interface. Significant differences between the solutions for AP and HTPB have been uncovered.

Future plans include the modeling of propellant cracks, including multi-dimensional effects recently observed in experimental studies at Los Alamos National Laboratory, in collaboration with B. Asay, S. Son and L. Berghout. In addition, they will examine multi-dimensional effects associated with stress concentrations generated by thermal expansion and phase change.

## Stability

There is strong experimental evidence that the flow in a rocket chamber can affect the burning of the propellant through mechanisms other than pressure imposition. These mechanisms are not well understood. It is possible that gradients generated by the interaction of acoustic waves with the steady-state injected flow can play an important role. Hegab has studied this in collaboration with David Kassoy of the University of Colorado at Boulder. The work addresses transient flow dynamics generated by time-dependent mass injection into the rocket chamber, with the goal of understanding the heat transfer and temperature dynamics that accompany co-existing acoustic and rotational velocity disturbances. Results for low Mach number, large Reynolds number flows reveal large transient temperature gradients at the sidewall and in the chamber interior. The associated large heat transfer to the surface may influence the combustion zone above the propellant.

Results for near-resonant frequency values show that temperature oscillations are approximately ten times greater than those for the non-resonant frequency. The time-dependent numerical data are used to calculate the mean axial velocity distribution across the chamber and RMS values of the velocity and vorticity fields, Figure 3.4.7. Future work will focus on the role that this physics might play in the context of *Rocfire*.

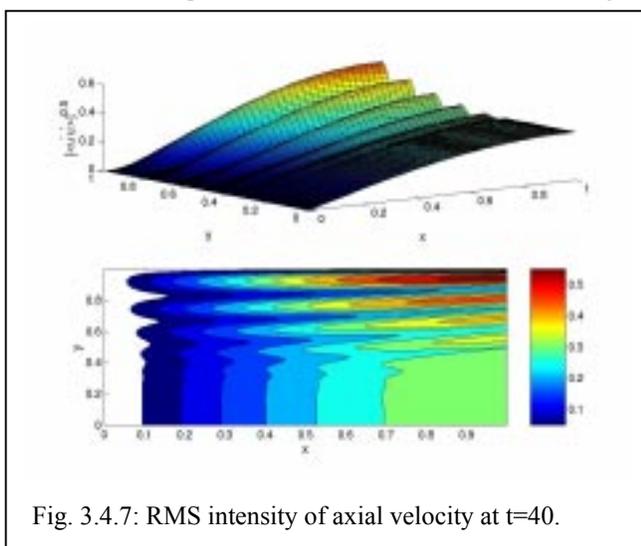


Fig. 3.4.7: RMS intensity of axial velocity at t=40.

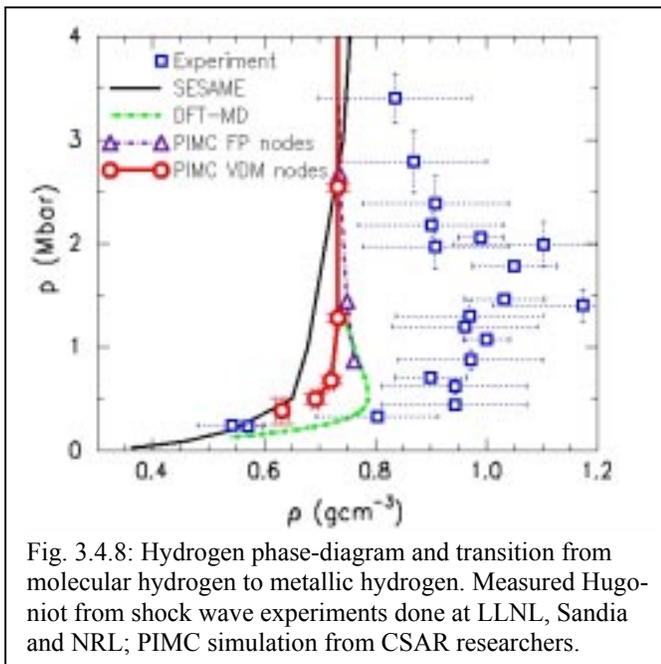
## Constitutive Modeling of Energetic Materials

A key challenge to the computational materials community is bridging the time- and length-scale chasm between atomistic behavior and continuum response. The determination of various macroscopic properties of a solid propellant—the macroscopic constitutive response—requires knowledge of the cohesive nature of the oxidizer/polymeric matrix interface. Capturing this information is beyond the scope and capabilities of continuum mechanics. This is partly due to the length scale involved in such phenomena (nanometers) and partly due to the phenomenological nature of the continuum theory that fails to establish criticality conditions based on local material thermodynamics and the actual deformation mechanism(s) operating at the atomistic level. Atomic scale simulation is an attractive analytical tool since the only physical input required is atomistic force fields, which can be accurately derived from quantum mechanical principles. Using either molecular dynamics simulations, in which the trajectories of all atoms are calculated simultaneously, or Monte Carlo methods, in which the phase space is sampled randomly, one can simulate the interface behavior under severe temperature and load conditions from the most fundamental point of view. Three CSAR subgroups are conducting such fundamental materials modeling research.

These efforts range from those directly investigating complex energetic molecules using methods that are relatively proven to those developing new methods and validating them on simpler systems.

### Path Integral Monte Carlo Methods

Ceperley and his students have developed, tested, and applied to dense hydrogen better methods to include fermion statistics in Path Integral Monte Carlo (PIMC). They have developed and tested a C++ version of their path integral code and an associated analysis workbench, allowing them to develop and maintain the code more easily and extend it to more complex materials. This includes methods that give a detailed understanding in a dense system of the number of bound states and their character. They have continued the study of the hydrogen phase-diagram and the nature of the transition from molecular hydrogen to metallic hydrogen. Shown in Figure 3.4.8 is a comparison of the measured Hugoniot from shock wave experiments done at LLNL, Sandia and NRL.



### First-principles Methods

Martínez and his students 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. This year, the accuracy of the methods has been demonstrated by direct comparison of simulations with experimental results for short time dynamics as probed by femtosecond spectroscopy. The product ratios, which are indicative of the accuracy of long time dynamics, have been computed for the photofragmentation of a combusive hydrocarbon molecule (ethylene). Simulation and experimental results are being compared. The first-principles dynamics methods have been extended to include tunneling effects that are important in the hydrogen atom and proton transfer reactions ubiquitous in combustion chemistry.

They have recently discovered a new model for describing charge transfer and polarization effects in atom-based molecular potentials. A key advantage that sets this method apart from others is that it both retains the simplicity of classical electrostatics and at the same time it is applicable when bond rearrangement occurs. Furthermore, they have shown that the new (quadratic valence bond) model is compatible with a multi-level treatment combining quantum chemical and classical electrostatic descriptions of different portions of a

molecular system. Implementation of this new method for general polyatomic molecules is in progress.

Finally, they are using first-principles methods to study the reaction of electronically excited OH radicals with H<sub>2</sub>. This is an important reaction in combustion applications because fluorescence of OH radicals is used as a spectroscopic probe of concentration during combustion. In the future they will continue work on hydrogen and hydrogen-helium mixtures in collaboration with Militzer, E. L. Pollock (LLNL) and Claus Heerlein (visitor from Germany) to produce a comprehensive equation of state; 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 calculate nuclear fusion rates in dense plasmas.

### Electron and Nuclei Calculation Methods

Martin's group is concerned with the development of theoretical approaches and efficient computational methods for the calculation of the properties of materials from the fundamental equations for the electrons and nuclei. Their goal in CSAR is to apply the general methods to prediction of the properties of energetic materials at high pressures and temperatures. Because the interesting physics and chemistry of energetic materials involve reactions and transformations, these present a challenging set of problems that require new developments of the computational algorithms and examination of the accuracy of the methods.

A computational scheme has been implemented in a code called *Siesta*, which incorporates the so-called order-N techniques for the solution of the electronic Hamiltonian. In contrast with the traditional methods where the scaling is cubic, here the CPU time and memory requirements scale only linearly with the total number of electrons (atoms) present in the simulation cell. Calculations with hundreds of atoms are therefore possible on single-processor workstations.

They have worked on the development of the parallel version of the *Siesta* method and the first production version of the program is now running on several platforms (Origin SGI, Cray T3E, cluster of DEC alpha workstations) showing good scalability, although improvements are still necessary. The method has been applied to the study of the equation of the state of nitrogen. Results are in good agreement with previous first-principles calculations performed with plane-waves methods (Figure 3.4.9). In particular, it has been confirmed that atomic phases

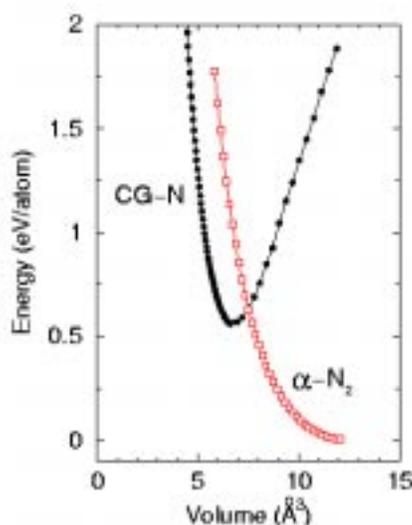


Fig. 3.4.9: Total energy versus volume curve for two different phases of solid nitrogen: cubic-gauche atomic phase, and alpha molecular phase. Figure shows that when pressure is increased, atomic structure becomes more favorable than molecular one. Data obtained with order-N scheme are in excellent agreement with those obtained with plane-waves by C. Mailhot et al. (Phys. Rev. B 46, 14419 (1992)).

where the molecules are dissociated should be more stable than the molecular ones for pressures higher than 30 GPa, even at low temperatures. This appears to be in disagreement with experimental observations, and they plan to investigate this long-standing discrepancy.

Future work will include the study of other molecular materials under high temperatures and pressures, especially hydrocarbons and materials containing C, N, H, and O.