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Challenges & Obstacles to Surmount

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On Beyond the Standard Model for High Explosives: Challenges & Obstacles to Surmount

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Abstract. Plastic-bonded explosives (PBX) are heterogeneous materials. Nevertheless, current explosive models treat them as homogeneous materials. To compensate, an empirically determined effective burn rate is used in place of a chemical reaction rate. A significant limitation of these models is that different burn parameters are needed for applications in different regimes; for example, shock initiation of a PBX at different initial temperatures or different initial densities. This is due to temperature fluctuations generated when a heterogeneous material is shock compressed. Localized regions of high temperatures are called hot spots. They dominate the reaction for shock initiation. The understanding of hot spot generation and their subsequent evolution has been limited by the inability to measure transients on small spatial ($\sim 1\,\mu$m) and small temporal (~ 1 ns) scales in the harsh environment of a detonation. With the advances in computing power, it is natural to try and gain an understanding of hot-spot initiation with numerical experiments based on meso-scale simulations that resolve material heterogeneities and utilize realistic chemical reaction rates. However, to capture the underlying physics correctly, such high resolution simulations will require more than fast computers with a large amount of memory. Here we discuss some of the issues that need to be addressed. These include dissipative mechanisms that generate hot spots, accurate thermal properties for the equations of state of the reactants and products, and controlling numerical entropy errors from shock impedance mismatches at material interfaces. The later can generate artificial hot spots and lead to premature reaction. Eliminating numerical hot spots is critical for shock initiation simulations due to the positive feedback between the energy release from reaction and the hydrodynamic flow.

Keywords: hot spots, shock initiation, detonation wave, plastic-bonded explosive, equation of state

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BACKGROUND

Plastic-bonded explosives (PBX) are an important class of solid high explosives. They are heterogeneous materials composed of explosive grains held together by a polymeric binder. In addition, a small amount of porosity (~ 1 per cent) is unavoidable. A micrograph of PBX 9501 is shown in fig. 1. We note that the grain size varies from about 5 to 400 μm and that the pores range in size from about 1 to 20 μm.

Detonation phenomena are affected by the heterogeneities in an explosive. A qualitative difference between a PBX and a homogeneous explosive (such as, liquid nitromethane) is observed in shock initi-

ation experiments; see [1, 2]. As seen in fig. 2, for the homogeneous case, thermal runaway at the interface initiates a detonation wave which then overtakes the lead shock. Whereas for a PBX, reaction behind the lead shock causes the shock strength to increase until a detonation wave forms downstream from the interface.

Propagation of a detonation waves is also affected by heterogeneities. Rate stick experiments show a qualitative difference of the curvature effect or detonation velocity as a function of diameter; see [3, 4]. As seen in fig. 3, for the homogeneous case, the detonation speed decreases approximately linearly with the inverse radius until failure occurs with a velocity
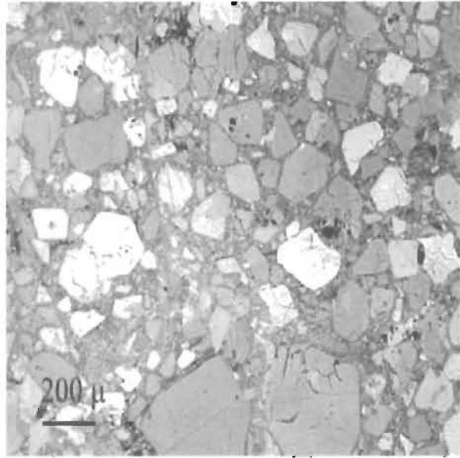
FIGURE 1. Polarized light micrograph of PBX 9501; from Skidmore et al. [6, fig. 4].

FIGURE 2. Wave trajectories and Lagrangian particle velocity histories for shock initiation: A. Homogeneous explosive and B. Heterogeneous explosive.

deficit of only a few per cent. Whereas for a PBX, the detonation speed shows a strong non-linearity with failure occurring after a velocity deficit of tens of per cent.

Another effect of heterogeneities is the phenomenon of shock desensitization, in which a weak shock can quench a propagating detonation wave in a PBX; see [5]. The desensitization is due to the weak shock squeezing out the pores. In fact, a single crystal behaves like a homogeneous explosive and is much less sensitive than a PBX.

Moreover, the nature of the heterogeneities makes a difference. Small variations with the formulation of a PBX (binder, grain size, and especially porosity) can have a large affect on initiation sensitivity. This is the result of temperature fluctuations, called 'hot spots', generated when a shock wave propagates in a heterogeneous material. Since chemical reaction rates are very sensitive to temperature, hot spots significantly affect the amount of reaction. Figure 4 illustrates this point. The measured time to detonation as a function of shock pressure is several orders of magnitude less than the reaction time based on the chemical reaction rate at the bulk shock temperature.

The importance of hot spots was recognized by the late 1940's; see [7] and references therein. But even after 60 years, the process by which hot spots lead to a detonation wave is not well understood.
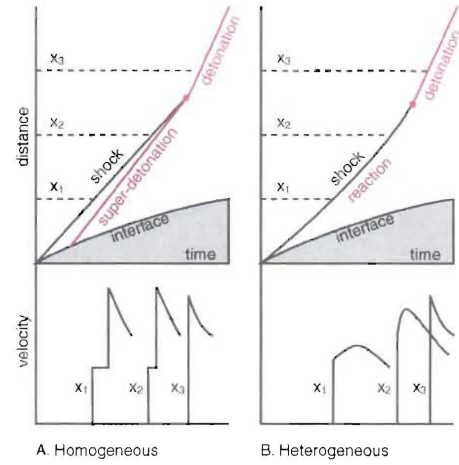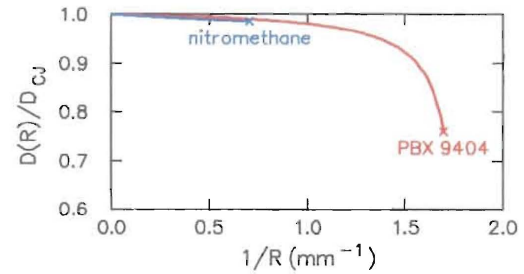

FIGURE 3. Diameter effect curve. Blue curve is homogeneous explosive liquid nitromethane. Red curve is heterogeneous explosive PBX 9404.
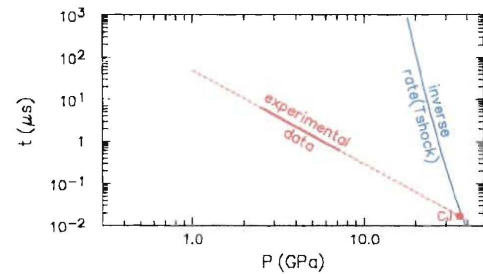

FIGURE 4. Time to detonation vs. shock pressure for PBX 9501. Red curve is experimental data [8]. Blue curve is inverse reaction time based on shock temperature and HMX 'global' Arrhenius rate of Henson et al. [9].
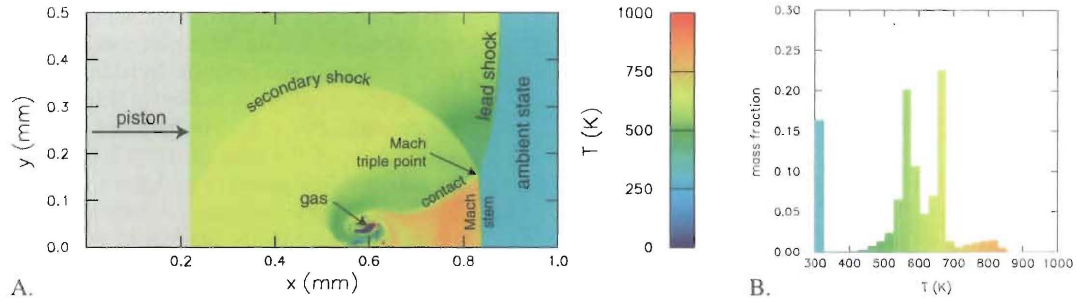
FIGURE 5. Temperature after pore collapse in HMX. Flow is driven by piston with velocity of 1.3 km/s and had only shock dissipation. Initial gas pore is circular, with center at $x = 0.4$ and $y = 0$, and radius of 0.1 mm. Top and bottom boundaries have zero normal velocity. A. 2-D temperature field. B. Temperature distribution. Fig. 3 of [10].

HOT SPOT CONCEPT

A hot spot is a small localized regions of high temperature. Unfortunately, there is very little data on the formation, evolution and interaction of hot spots. This is due to the limited resolution of diagnostic techniques. Detonation wave experiments measure the collective effect of a large number of hot spots, rather than an individual hot spot, which in a PBX has spatial and temporal scales on the order of 1 micron and 1 ns, respectively. It is noteworthy that the size of a hot spot is much less than the reaction zone width of a steady detonation wave. Consequently, a single hot spot can not initiate a detonation wave.

Moreover, there are multiple physical scales (grain size, reaction rate, acoustic transit time, heat conduction, dissipative mechanism) leading to several dimensionless parameters. As a result, one can not simply scale the heterogeneity such that the hot spots are large enough to measure. In addition, one has one shot before the sample goes up in smoke, that is, one does not have the luxury of pulsing a laser and adjusting the alignment and timing of the diagnostics.

Many mechanisms to generate hot spots have been proposed, see [11] and references therein. For a PBX, the sensitivity of shock initiation to porosity, implies that hot-spot formation is dominated by void collapse. Formation of a hot spot requires a dissipative mechanism. For hydrodynamic void collapse, shock heating is the only dissipative mechanism. An illustration of the temperature field after a shock driven void collapse is shown in fig. 5.

It is noteworthy that the region of high temperature is not uniform. Rather, a hot spot corresponds to the tail of the temperature distribution. With an additional dissipative mechanism, such as shear viscosity, the tail would extend to higher temperatures. The tail will also depend on shock strength and to some extent the shape of the pore.

Hot spots have a much smaller induction time than the bulk of a shocked explosive. Hence, they react on a much shorter time scale then the rest of the explosive. The ignition of a hot spot leads to a high temperature and generates a deflagration wave propagating outward from the reacted hot spot. This is the 'ignition & growth' concept [12] that is used as a heuristic for many burn models. Moreover, the energy release leads to higher pressures that are acoustically coupled to the shock front. The positive feedback leads to the buildup of a detonation wave as shown in fig. 2.

Based on ignition & growth concept, the average burn rate would be

$$Rate = (\text{surface area}) \times (\text{deflagration speed}) .$$

In general, the average burn rate depends on the hot-spot distribution. Qualitatively, the surface area is proportional to the number of hot spots and a geometric factor that is a function of the amount of reacted material, which we denote by λ. Both the deflagration speed and the number of hot spots are expected to be functions of pressure. Hence, the average burn rate would be a function of P and λ. In contrast, a chemical reaction rate for a homogeneous explosive is a function of T and λ.
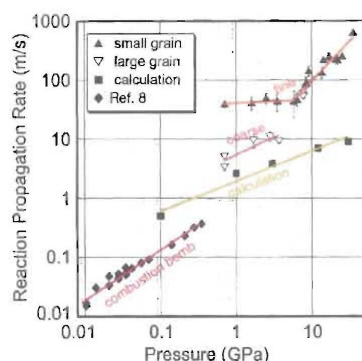
FIGURE 6. Deflagration speed vs. pressure for HMX; from Esposito et al. [13, fig. 5]. The highest pressure point corresponds to the CJ pressure of PBX 9501, 35 GPa. But the deflagration speed is lower than the CJ detonation speed of 8.8 km/s.

There is however a quantitative difficulty with the ignition & growth concept. Experiments have shown that the deflagration speed is a function of P; see fig. 6. Even at the CJ pressure, the deflagration speed is much smaller than the detonation speed. Consequently, a large number of very small hot spots would be needed for the time-to-detonation of shock initiation shown in fig. 4. This is not consistent with the pore distribution inferred from the micrograph shown in fig. 1.

STANDARD MODEL CLASS

The cell size for numerical simulations is typically greater than the grain size. Consequently, a model is needed in which the PBX is homogenized and an effective burn rate used to account for the sub-grid reaction due to the hot spots. This is reasonable since initiation and propagation of a detonation wave is due to the collective effect of a large number of hot spots and is very reproducible.

Specifically, a partly burned PBX is treated as a mixture of reactants and products. The mass fraction of the products, λ, is taken as a reaction progress variable. The evolution of the PBX is governed by the fluid equations for mass, momentum & energy conservation, and a rate equation for λ. The fluid flow is coupled to the reaction through the dependence of the fluid pressure on λ.

For the 'standard' class of initiation model, separate equations of state (EOS) are used to characterize the reactants and products. In addition, pressure-temperature equilibrium is used to determine a mixture pressure, $P(V, e, \lambda)$. The burn rate represents the cell average of the reaction from hot spots. Since the hot-spot distribution is not known, a fitting form is assumed and its parameters calibrated to experiments. Motivated by the ignition & growth concept, the rate is taken as function of P and λ.

As an aside, the ignition & growth concept implies that the reactants and the products are phase separated by a deflagration front. Therefore, temperature equilibrium would not be a good approximation. Moreover, pressure equilibrium would only be a good approximation to the extent that the speed of the deflagration front is small. Different temperatures for the reactants and products would require a two-phase fluid model; see for example [14] and references therein. This has been tried for granular explosives, and more recently in the CREST model [15] for a PBX. Two-phase models have issues with shock waves that have not yet been fully resolved.

Examples of the standard class of model are Forest Fire [16], and Ignition & Growth [12]. These models were formulated in the 1970's. Extensions of these and subsequent initiation models have the same general character and are mostly a variation on a theme. Typically, these models are calibrated with 1-D shock-to-detonation experiments. Burn parameters are adjusted to fit distance-of-run to detonation data (known as a Pop-plot) or velocity gauge data.

Models of the standard class have been used for both initiation and propagation of a detonation wave. Another type of model, called Detonation Shock Dynamics (DSD), aims at reproducing the curvature effect, *i.e.*, the variation of the detonation speed with front curvature; see [17]. It applies to quasi-steady propagation of a detonation wave. The basic assumptions of DSD preclude its use for shock initiation.

There is a tacit assumption in a standard burn model; namely, the hot-spot distribution corresponds to that in the calibration experiments. Consequently, the domain of applicability is limited. A model works well for applications that are similar to the calibration experiments but are not accurate in other cases. One limitation is that different burn parameters are needed when the initial temperature or initial density of a PBX is varied. There are also difficulties

with ramp wave rather than shock wave loading, and 2-D problems in which side rarefactions lead to dead zones or failure. Moreover, for accident scenarios and safety issues which involve thresholds for initiation, the standard class of model is not predictive.

UNDERSTANDING HOT SPOTS

To develop reactive models for heterogeneous explosives that encompass a wider range of applications, a better understanding of hot spots is needed. Physical experiments do not have the required resolution. An alternative is to use numerical experiments based on meso-scale simulations, that is, continuum mechanics simulations that resolve heterogeneities and hot-spot reaction. Of course, such numerical experiments have been performed previously; see for example, Mader [18, sec. 3.3]. However, the resolution of earlier simulations were limited by the computers of the day. With the increased computer power — both speed and memory — now available, it is worthwhile to try again.

Good numerical experiments will take more than just raw computing power. Since the idea is to compute reaction from hot spots, simulations need to use a chemical reaction rate. Chemical rates are sensitive to temperature and require EOS models with better thermal properties then currently used with the standard pressure based empirical burn models. Typically, EOS models for the solid reactants assume that specific heat is constant. Since explosives are large molecules with many internal vibrational degrees of freedom, the specific heat has a significant temperature variation in the regime of interest for shock initiation; see fig. 7.

In addition, several numerical issues need to be addressed. The following are the most important:

1. Shock capturing codes incorporate numerical dissipation from either artificial viscosity or approximate Riemann solvers. Additional dissipative mechanism may be required for hot-spot formation.

2. Typically, hot spots form near material interfaces where numerical errors are largest. For example, transients due to shock impedance mismatches give rise to entropy errors that are manifested as temperature errors near interfaces. This can artificially trigger reaction and would be disastrous for initiation studies.
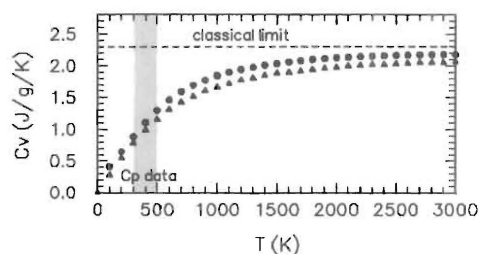

FIGURE 7. Specific heat for β-HMX. Triangle symbols are from molecular dynamics calculations [19, fig. 4.13], and circle symbols from vibrational frequencies in [20, tables 2 and 3]. C_p data (at atmospheric pressure) is limited to the gray region. Dotted black line is the classical limit.

3. Artificial stationary burn fronts can occur for Eulerian algorithms needed to handle large grid distortions. They result from advection of reactants into a burned cell. The P-T equilibrium mixture EOS raises the temperature and causes the reactants to burn. Instead, there should be a deflagration front which is slow moving relative to the flow.

4. Deflagration fronts are subsonic and driven by heat conduction. They must either be tracked or the profile resolved. Due to the small value of the thermal diffusion coefficient, very high resolution would be needed. In addition, the P^n dependence of the deflagration speed shown in fig. 6 requires a second reaction step for vaporization of pyrolysis.

Possibly, a more sophisticated use of adaptive mesh refinement can be used to mitigate these issues.

To start out, I think some simple numerical experiments are needed. An illustrative example is aimed at understanding what the hot-spot mechanism is for an initiation experiment in which known heterogeneities (glass micro-beads) are introduced into a homogeneous explosive (liquid nitromethane); see [4, 21]. The pressure field in fig. 8 shows that there are lots of reflected waves. However, the peak temperatures are due to transverse waves set up along the lead shock front.

This example suggests an alternative to the ignition & growth concept. Thermal ignition of a hot spot will generate a pressure pulse which catches up to the lead front and generates additional transverse wave. These waves generate new hots spots at the shock front which after an induction time will ignite. Perhaps it is this mechanism for generating new
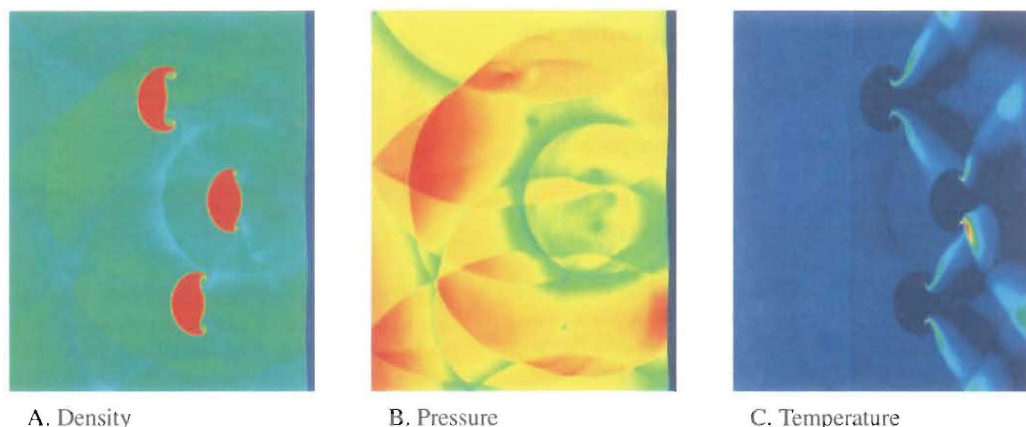
A. Density   B. Pressure   C. Temperature

FIGURE 8. Simulation of shock in nitromethane interacting with glass beads. Computational domain is 120×150 microns. Initially, glass beads were circles, 20 microns in diameter. A 10 GPa shock is driven by inflow at left boundary and has propagated just short of the right boundary after 25 ns. Top and bottom boundaries are rigid walls.

hot spots that dominates the reaction over the growth phase due to slow deflagration waves.

MATERIAL PROPERTIES

Equations of state are a key input for a numerical simulation. For a specific material, more than one model can be found in the literature. There can be significant differences among models. Moreover, the accuracy and domain of a model is often not stated. Extrapolating outside the domain can lead to large errors.

To illustrate these points, three models for the reactants of PBX 9501 are compared. The three models are all of the Mie-Grüneisen form and fit to high pressure data from either shock wave experiments or diamond anvil experiments. But they use different fitting forms for the pressure and different assumptions for the specific heat. A comparison of the principal Hugoniot locus for the three models is shown in fig. 9.

The green model used a linear $u_s - u_p$ fit for the Hugoniot locus but did not include the three high pressure single crystal HMX data points. We observe a significant difference of 30% in the particle velocity at a shock velocity equal to the CJ detonation speed. This in turn leads to a large difference for the von Neumann spike pressure of a ZND detonation wave. In fact, for the green model, the reactant locus crosses the detonation locus only slightly above the CJ pressure. While this does not violate physical principles, it is suspect, and would affect the structure and perhaps stability of overdriven detonation waves. Also, we observe that the red and green models have similar shock temperatures. However, this is due to a compensation of errors between the specific heat and the Hugoniot energy $(= \frac{1}{2}u_p^2)$.

It is also interesting to compare the P-T equilibrium mixture EOS for partly burned PBX. For the three models, fig. 10 shows the pressure, temperature and component densities as a function of mass fraction for fixed (V, e) corresponding to the CJ state. Again we observe that there are significant difference among the models.

For a similar variation with λ at fixed (V_0, e_0), one of the models fails to have a P-T equilibrium solution for $\lambda \gtrsim 0.9$. This is due to exceeding the domain of the reactant EOS (isothermal compressibility failing to be positive) when V is a little larger than V_0. This is a generic problem for solid EOS, which have been developed for compression. It emphasizes the importance of knowing the domain, and staying within it.

Empirical fits for the burn rate can compensate for errors in the reactant EOS. However, the differences in the EOS shown in this example would have a large effect on initiation simulations in which hot spots are resolved and chemical reaction rates are used.
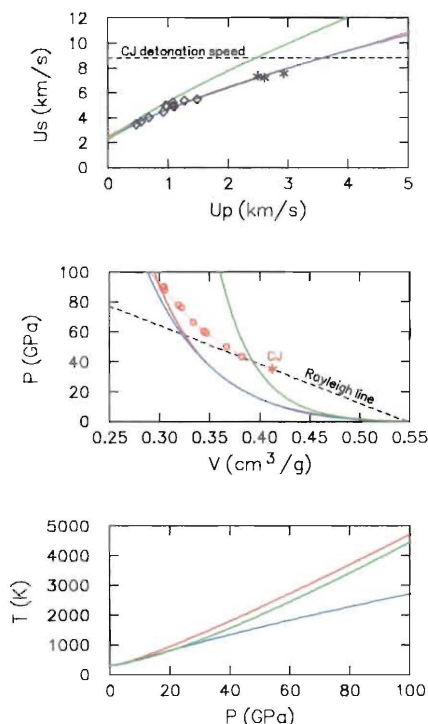
FIGURE 9. Comparison of reactant PBX 9501 Hugoniot loci for three models. Symbols in (Up, Us)–plane are experimental data points. Dashed black line in $(V.P)$–plane is the Rayleigh line through the CJ state, indicated by star. Dotted red curve is overdriven detonation locus, and symbols are experimental data points. Fig. 1 of [22].

FIGURE 10. Variation with reaction progress variable of pressure, temperature, and specific volumes of reactants and products, for partially burned PBX 9501 at fixed $(V.e)$ corresponding to CJ point. Plot of specific volume shows curves for both reactants and products (long-dashed, short-dashed and dot-dot-dash). Fig. 9 of [22].

CHALLENGES & OBSTACLES

To summarize, the difficulty with modeling heterogeneous high explosives is due to the fact that the reaction is dominated by hot spots or fluctuations in the temperature field rather than a coarse grain average or mean temperature field. Standard models for explosives use an empirically determined burn rate which tacitly assumes that the hot-spot distribution is the same as the calibration experiments. Past attempts to improve the fitting form used for the burn rate have had limited success.

The real modeling challenge — to extend the range of applicability of burn models — is to account dynamically for changes in the hot-spot distribution. Additional state variables would be required to char-
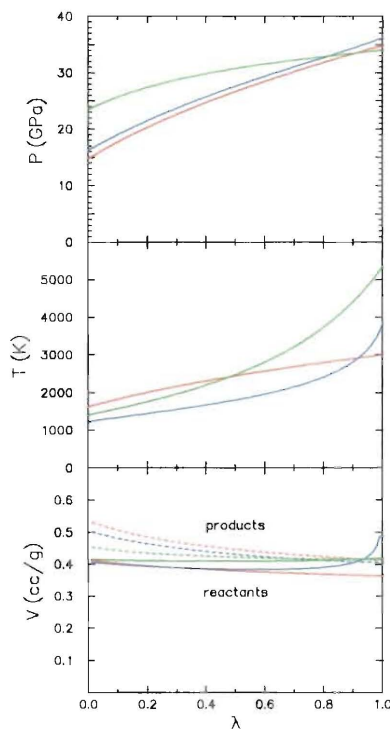
acterize the hot-spot distribution along with governing equations for the new variables. This is analogous to what is done for material strength models; extending elastic flow to account for hysteresis effects by adding state variables for plastic strain and work hardening degrees of freedom.

To go beyond the standard model class, a needed first step is to obtain data on the formation, evolution and interaction of a small number of hot spots. Until diagnostic techniques obtain the required resolution, the data can only come from numerical experiments. Due to the positive feedback between the energy release and the fluid flow, reactive simulations are more sensitive to numerical errors than for non-reactive hydrodynamics. Addressing numerical issues adds to the challenge.

In addition, numerical simulations require material properties as input. Equation of state data and model parameters for a specific material are scattered through the literature. For a particular explosive, finding all the available data and assessing the different models is very time consuming. This is an unnecessary obstacle that slows down and impedes progress.

It would help if the research community organizes to take advantage of the technology made available by PCs and the Internet. In particular, an on-line database for high pressure material properties would benefit the entire research community. It would greatly facilitate comparing models with data and with each other. Hopefully, this would result in higher quality material models that are needed for high resolution simulations used to understand physical phenomena at shorter length scales.

ACKNOWLEDGMENTS

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