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Isochoric Burn, An Internally Consistent Method for the Reactant to Product Transformation in Reactive Flow

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ISOCHORIC BURN, AN INTERNALLY CONSISTENT METHOD FOR THE REACTANT TO PRODUCT TRANSFORMATION IN REACTIVE FLOW

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Mixture rules for partially reacted explosives differ amongst various models. For instance, JWL++ uses a partial pressure addition to compute an average zonal pressure, Ignition and Growth requires pressure equilibration and thermal equilibration of temperature dependent JWL EOSs, CHEETAH In Line RF also assumes temperature and pressure equilibration. It has been suggested in the past that a more realistic equilibration scheme should comprise isentropic pressure equilibration of the separate reacted and unreacted phases. This turns out not to be a proper path for equilibration. Rather, we find that the only internally consistent method is the evaluation of the equilibrium pressure that satisfies the particular conditions of reactant and product resulting from deflagration in a fixed volume.

INTRODUCTION

The method of solving the mixture EOS is central to the application of reactive flow in hydrodynamic simulations of explosive response. The characteristic of reactive flow models that sets them apart from lighting-time schemes is the inclusion of reactant, reacted explosive, and their mixture in the initiation and propagation process. It is important, therefore, to establish an internally self-consistent method to carry out the burning (transformation) process. A number of methods have been employed to reach local pressure equilibration of the mixed phases in reactive flow models.[1-4] These include temperature equilibration,[2-4] partial pressure summation,[1] and isentropic pressure equilibration. If we subscribe to the generally accepted description that the physical process in reactive shocks in explosives is the deflagration of numerous small regions behind the shock wave, it becomes clear that none of these methods actually apply and in some cases are poor approximations. We will show that transformation and heat release in a fixed volume, "isochoric burn", can be formulated in a manner which is internally consistent and which provides an effective method for the pressure equilibration.

For many problems the reactive processes take place at or near the steady propagation of a detonation and therefore at high pressure. In these cases calculational results may not deviate strongly from one method to another. This is primarily because the thermal component of pressure as described in the equations of state used in most hydrodynamic calculations is a small correction to the "cold" compression component, which describes the repulsion of gas molecules in close proximity. However, for low-density explosions, where the fraction burned is small and the thermal component is large, the mixture pressure estimation methods can vary significantly.

The constraint of thermal equilibrium can be a source of computational problems in reactive flow calculations where chemical equilibrium calculations are applied to the products[4] since products brought into equilibrium with "cold" reactant will be at much lower temperature than is realistic especially for small values of the burn fraction. Moreover the equations of state used in chemical equilibrium calculations display a more realistic and much larger thermal contribution to the pressure.

We have carried out hydrodynamic calculations of deflagration in a fixed volume to establish the thermodynamic state and have incorporated isochoric burn (IB) pressure equilibration in the Ignition and Growth (I&G)[2] model. Calculations with these models show a number of important

differences from previous pressure equilibration methods and illustrate the advantages to the IB equilibration.

THE PHYSICAL MODEL

The following is based on the widely accepted premise that the burn process is just as described above, a deflagration of the reactant explosive following ignition by a shock wave. The physical model for the process once ignited can be described as a multitude of microscopic deflagrations distributed uniformly within a zone. Because the burn regions are microscopic the flame rates can be subsonic and still consume the explosive in times consistent with observed reaction times. The flame speeds have been measured at high pressure in Diamond Anvil Cell experiments for a few explosives.[5-8] For HMX[8] the measured flame speed at high pressure (5 to 40 GPa) is given by $1.05P^{1.73}$ for pressure in GPa and the flame speed in m/s. At 35 GPa, the approximate Chapman-Jouget pressure for many HMX-based explosives, the flame speed is 490 m/s. This is well below the detonation speed of 8600 m/s. If the reaction zone is of order 0.2 mm, then the average effective hot-spot separation must be about 20 μm. (The flames from two adjacent hot-spots must meet in the middle in the time that the detonation front traverses the reaction zone.) Given the measured flame speed, if the hot-spot separation were less than 20 μm, then the reaction zone would be smaller than measured. If more, then the reaction zone would be larger.

The flame fronts are very thin at high pressure. Our (unpublished) direct numerical simulations of flame propagation at high-pressure exhibit flame thickness of less than 100 nm at 12 GPa, and even thinner flames at higher pressure. Because our simulations result in flame speeds that are less than measured, our calculated flame thickness is an overestimate. A thin flame, in turn requires that the bulk of the unreacted explosive be at low temperature relative to the burned explosive. For plastic bonded or cast explosives with nominal porosity, the unreacted temperature is that associated with a shock in fully dense material, from 300 to 1000K, depending on the shock pressure.

It follows from the deflagration description that the reactant and product are in pressure equilibrium but not in thermal equilibrium. Thus the thermal equilibration used by Ignition and Growth and by the current CHEETAH models are not consistent with a deflagration description. Also, to the extent that the volume is constant, the equilibration process cannot be isentropic in both the products and reactant. The reasoning is as follows. The volume change for the two phases must be equal and opposite to conserve the total volume. The pressure in the product phase is greater until equilibration is achieved. In an isentropic process for each species i,

$$dE_i = -PdV_i$$

so that

$$\left|dE_{product}\right| > \left|dE_{reactant}\right|,$$

which violates

$$dE_{total} = 0 + qdm,$$

where q is the energy density released by the reaction step involving the incremental mass, dm. The conservation of energy for a constant-volume process is easier to write for the case in which the product gasses do not add energy to the system, but rather have a differing energy of formation. This is the customary view of chemical calculations. In the customary view of hydrodynamic calculations, the conversion of reaction to product is accomplished with an addition of energy to the system, as above, which is proportional to the mass converted. The two methods are equivalent, so long as one remembers which convention is being followed. Other methods for mixture rules, such as fraction-weighted pressure addition, are approximations that also do not correspond to the meso-scale description and in general do not conserve internal energy in the zone.

Consider the finite differencing employed in hydrodynamic computation. A finite fraction of the total high explosive energy is added to a zone over the hydrodynamic time-step dt as the reactive process advances. We think of the deflagration process and energy release as proceeding as a continuous. The problem therefore is to determine the condition in the zone due to a continuous release throughout the finite time-step imposed by the hydrodynamic computation. There is an internally consistent method for solving this problem. The sequence in hydrodynamic differencing is that at each time step in each reacting zone a fraction of the explosive is converted to product with the zone volume held constant throughout that step. Once the equilibrated pressure is determined, the zone pressure, energy, and volume are revised consistent

with momentum and energy exchange with adjacent zones.

The appropriate procedure became clear when we carried out "sub-zonal" hydrodynamic calculations using ONEDEE,[9,10] which simulated the continuous deflagration of 30% of the explosive by a time evolving volume burn of one section comprising 30% of a "zone" volume filled with explosive. To simplify the analysis our initial calculations used gamma law gas equation of states (EOS) for both reactant and product. The actual volume for the hydrodynamic calculation was a 100-μm cube.

The burn velocity in the volume was chosen arbitrarily, but is similar to that for laminar flame speeds in explosives at modest pressure (>10 m/s). The results showed, as demanded by thermodynamics, that the total internal energy of the volume was conserved since the volume of the zone is unchanged. The time evolution of pressure and the phase boundary for the sub-zonal calculation are shown in Figs. 1 and 2. The small oscillations are due to wave reverberations within the hydrodynamic volume. The hydrodynamic wave speed for this case is about 4000 m/s. The crucial observation was that for subsonic flame rates the volume of the compressed reactant phase is given by the isentropic compression of the reactant phase from the initial volume and pressure to the final pressure. Cowperthwaite[11] utilized this same assumption in his model earlier. This is illustrated also in Fig. 1 by comparison of the isentropic compression of the reactant from the initial to final state with the pressure history in the reactant. As one would expect, if the full 30% of the explosive is burned instantaneously or at rates near sonic speed, the result (not shown) is no longer isentropic compression but rather shock compression of the reactant phase.

In these one-dimensional simulations, which do not include mixing of the gas products, there is a gradient of product temperature and internal energy density, although pressure equilibrium obtains accurately. This is easy to understand. The first conversion of reactant to product takes place at the initial pressure of the reactant. The last conversion takes place at the final pressure, which is considerably higher. The previously converted gas is compressed adiabatically to the new pressure, as the last portion expands to pressure equilibrium. The thermodynamic constraint of constant energy (see above) is maintained. The internal energy density profiles at the beginning and at the end of the burn are shown in Fig. 3.

The resulting two-part analytic procedure is as follows. First the hydrodynamic zone is equilibrated to the new change in volume assuming equal pressure and equal artificial viscosity for reactant and product, with no change in composition. This is the initial state. Then a finite mass transformation and energy release at constant zone volume determines the energy, pressure, and volume for reactant and product phases. The reactant, reduced by the mass conversion, lies on its compressed isentrope. The expanded product is constrained to conserve energy and volume.

$$E = E_{react,fin} + E_{prod,fin} = E_{reac,init} + E_{prod,init} + q dm$$

$$E = \frac{PV_{reac,fin}}{\gamma_{reac} - 1} + \frac{PV_{prod,fin}}{\gamma_{prod} - 1}$$

$$V_{reac,fin} + V_{prod,fin} = \text{const.}$$

$$V_{reac,fin} = V_{reac,init}\left(\frac{P_{init}}{P_{fin}}\right)^{\gamma_{reac}}$$

EFFECT OF THE PRODUCT EQUATION OF STATE

We incorporated the above model in an Ignition and Growth model in ONEDEE. As others have noted,[12] there are only minor differences between the IB results and the standard I&G results when we applied the models to typical HMX-based explosives using the JWL equation of state for the products. Recent calculations with CHEETAH and with CHEQ[13] have been compiled as tabular equations of state for the products of HMX decomposition. Although the CJ adiabats for the two calculations are nearly as good a representation of experiments as are the JWL equations of state that have been fit to cylinder tests,[14] the behavior away from the CJ adiabat is quite different. The thermal component of pressure, F_T, we define to be

$$F_T(\rho) = \frac{P(T,\rho) - P(T_0,\rho)}{P(T,\rho)}.$$

The value of F_T for a tabular equation of state from CHEETAH and for the JWL equation of state,[15] both of which represent HMX, are shown in Fig. 4. At very high density, for both equations of state, the thermal component is small. For low

density for both equations of state, the thermal fraction is large. (To the extent that the equation of state approaches that of an ideal gas, the thermal component should be 1.0) At intermediate density, where the build-up to detonation occurs, the two fractions differ dramatically.

We carried out calculations of the transformation of HMX from reactant to product using two different ALE 3D models developed by Nichols[16] for modeling chemical materials. The first exhibits thermal equilibrium between reactant and product, in imitation of the standard I&G models. The second models a deflagration with a thin flame front and prevents thermal equilibration between the species. It uses a level-set method to separate burned from unburned explosive. We applied these two models to deflagrations that start with the reactant at 10 GPa, 500K, which represents a state in the build-up to detonation from a low-pressure shock. The reactant density at that condition is 2.57 g/cm^3. The results are shown in Figs 5 and 6 for the JWL and CHEETAH equations of state. The JWL results are very nearly the same, whether thermal equilibrium is enforced or not. The CHEETAH equation of state results are significantly different. At initial density near the reactant's initial density of 1.9 g/cm^3, the differences exhibited in Fig.5 are expected to be even larger, because the thermal component is larger (Fig. 4).

CONCLUSIONS

The analyses presented here demonstrate that single temperature descriptions of reacting materials under shock loading are inadequate to describe real systems in which thermal equilibration times are much greater than the reaction times and pressure equilibration times. The development of a capability to handle multi-temperature systems allows realistic equations of state and consistent thermodynamics to be applied to reacting systems in particular and to mixtures in general.

It is important to emphasize that in analyzing reacting systems where only a portion of the potential heat release occurs, a serious error may very well be introduced by imposing thermal equilibrium.

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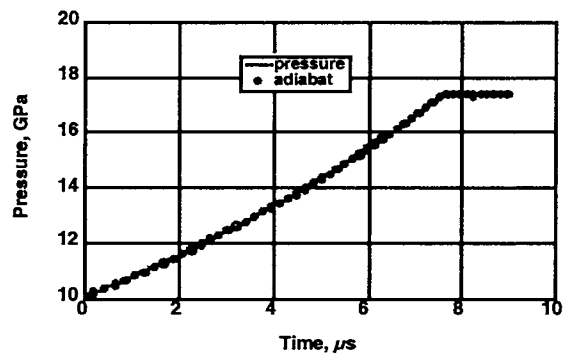

Figure 1. Evolution of pressure in a deflagrating explosive modeled by gamma-law gas for both the product and the reactant (line). Open circles are the reactant adiabat from the initial pressure

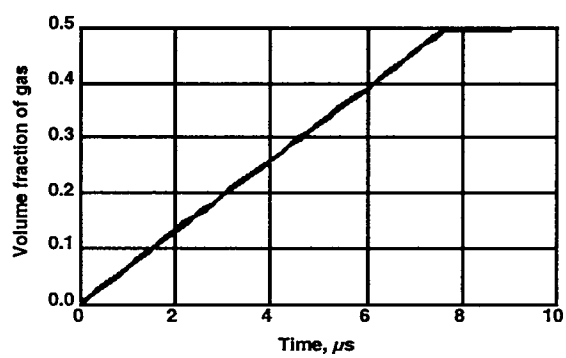

Figure 2. Location of the deflagration interface as the deflagration proceeds. The volume fraction of burned explosive is almost 0.5, although the mass fraction is 0.3

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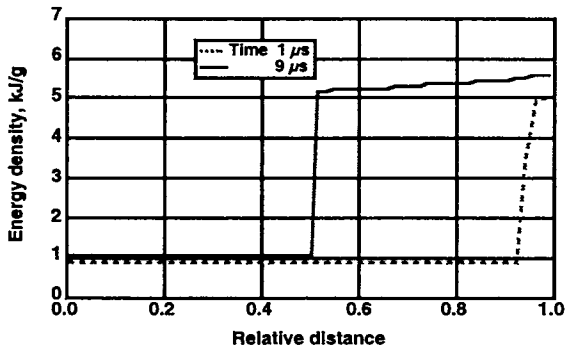

Figure 3. Energy density profiles at the beginning (dash) and end (solid) of deflagration. The energy density of both the reactant and product change during the deflagration.

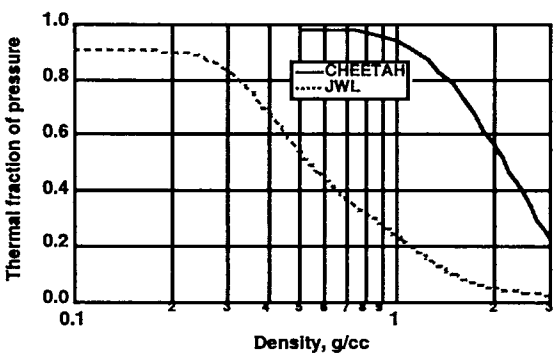

Figure 4. Fraction of the pressure due to the thermal component for the JWL equation of state (dash) and the CHEETAH equation of state (solid). Normal density is 1.90 The deflagrations for 10 GPa start at density 2.57.

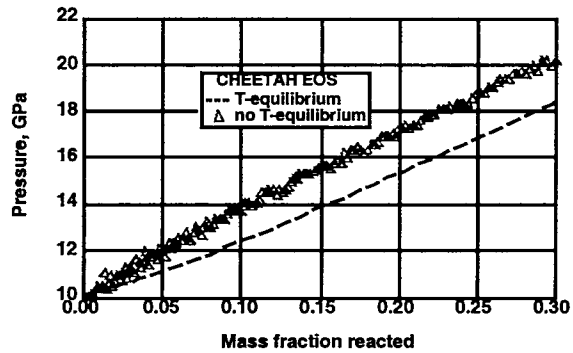

Figure 5. Pressure as a function of mass fraction converted to product for the CHEETAH equation of state for the case of thermal equilibrium (I&G, dashed) and non-equilibrium (IB, symbol)

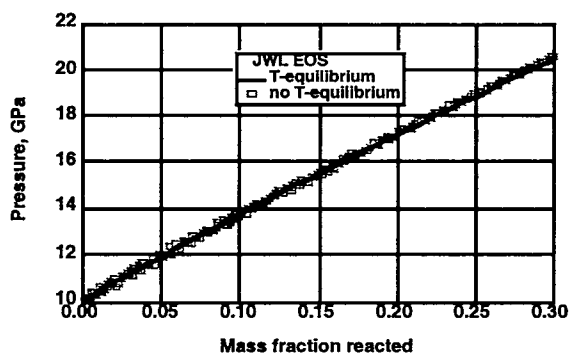

Figure 6. Pressure as a function of mass fraction converted to product for the JWL equation of state, for the case of thermal equilibrium (I&G, solid) and non-equilibrium (IB, symbol)

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