

EQUATION OF STATE FOR MODELING THE DETONATION REACTION ZONE

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We present an equation of state for modeling the detonation reaction zone that is based on earlier work of Davis that developed equations of state for the reactants and products separately. This work presents a plausible way to combine the two to form a hydrodynamic equation of state that is linear in both the pressure and specific internal energy and a single reaction progress variable. The limiting form of the reactant and product equation of state fits available experimental data. We examine the different closure models for a simple mixture theory that interpolates between the reactant and product EOS.

INTRODUCTION

The reaction zone of a detonating high explosive is a complicated region. When the explosive is partly consumed, there is a mixture of unreacted explosive and reaction products, so one can imagine particles of explosive surrounded by products and that the particles are reacting in a thin layer at their surfaces. Alternatively, there might be small volumes of products within particles of reactants with reaction at the surfaces. Modeling such a complicated system can be accomplished only by making some very restrictive assumptions.

The standard assumptions, which are made here, are:

1. The detonation is plane and steady.
2. The pressure has the same value in the reactants and products.
3. The particle velocity of the reactants and products are the same; there is no flow of products past the reactants.
4. Equations of state for both reactants and

products are known.

5. There is ideal mixing of reactants and products.
6. The material is either reactants or products; intermediates are not considered.
7. One reaction progress variable is sufficient to describe the process.

The usual conservation laws applied with the listed assumptions give the total specific internal energy of the mixture, but no information about how that energy is apportioned between the reactants and the products [1, 2]. Another assumption is needed. Two limiting cases are considered in this paper:

1. The reactants and the products are in thermal equilibrium; the energy liberated in the reaction is apportioned so that the temperature is the same in reactants and products.
2. All the energy liberated in the reaction stays in the products; there is no transfer of heat to the reactants.

In the real physical detonation the energy will be apportioned in a fashion somewhere between these limiting cases. For example, it may be that near the von Neumann point where little reaction has taken place limiting Case 2 is a good approximation. And then near the CJ point, where most of the reaction is complete and reactant particles are very small, limiting Case 1 may be approached. If so, some model for going from one limit to the other is needed.

While only the plane, steady detonation is considered in this paper, the goal must be to find a method for making a satisfactory mixture equation of state that will reproduce dynamic behavior over a wide range, from detonation to shock initiation, and flows with large curvature. In addition, it is desired that the equation of state be efficient to implement in large-scale numerical simulations. Mixture equations of state usually require iteration to solve for the state variables that go with the assumed apportioning of internal energy. An algebraic approximation that makes the iteration unnecessary is required to make the mixture equation of state useful for routine problems.

EOS FOR PRODUCTS

The products EOS is taken from [3] without change. It is given by

$$E_p(p, v) = E_p^S(v) + \frac{v}{\Gamma_p(v)} [p - p_p^S(v)] \quad (1)$$

where E is the specific internal energy, p is the pressure, and v is the specific volume. The subscript p denotes the products, and the superscript S indicates that the function is defined on an isentrope. The isentrope used is the principal isentrope, the one that passes through the CJ point. It is given by

$$p_p^S(v) = p_c \frac{[\frac{1}{2}(v/v_c)^n + \frac{1}{2}(v/v_c)^{-n}]^{a/n}}{(v/v_c)^{k+a}} \times \frac{k-1+F(v)}{k-1+a} \quad (2)$$

$$F(v) = \frac{2a(v/v_c)^{-n}}{(v/v_c)^n + (v/v_c)^{-n}} \quad (3)$$

$$E_p^S(v) = E_c \frac{[\frac{1}{2}(v/v_c)^n + \frac{1}{2}(v/v_c)^{-n}]^{a/n}}{(v/v_c)^{k+a-1}} \quad (4)$$

$$E_c = (p_c v_c)/(k-1+a) \quad (5)$$

$$\Gamma_p(v) = k-1+(1-b)F(v) \quad (6)$$

The constants p_c , v_c , a , n , k , b are found by calibration to experimental data.

EOS FOR REACTANTS

The EOS for the unreacted explosive, the reactants, is a modification of an EOS given in [4]. The subscript r denotes the reactants. The EOS is given by

$$E_r(p, v) = E_r^S(v) + \frac{v}{\Gamma_r(v)} [p - p_r^S(v)] \quad (7)$$

The reference isentrope, unmodified, was

$$p_r^S(v) = \hat{p} [\exp(4By) - 1] \quad (8)$$

where $y = 1 - v/v_0$, $v_0 = 1/\rho_0$ is the initial specific volume, $\hat{p} = \rho_0 A^2/4B$, and A and B are determined from measurements of the Hugoniot curve. The modified reference isentrope is

$$p_r^S(v) = \hat{p} \left[\sum_{j=1}^4 \frac{(4By)^j}{j!} + C \frac{(4By)^5}{5!} \right] \quad (9)$$

This new reference isentrope is a truncated expansion of the original. The Hugoniot curve found using the original isentrope intersects the detonation Hugoniot curve for the products at high pressure. The experimental data are at low pressure, corresponding to small values of y . The Hugoniot curve found from the new form does not intersect the products Hugoniot curve. The constant C allows adjustment of the reactants Hugoniot curve at high pressure.

The energy on the isentrope is found from the thermodynamic identity $(\partial E / \partial v)_S = -p$ so we have

$$E_r^S(v) = v_0 \int_0^y p_r^S(\bar{y}) d\bar{y} + E_0 \quad (10)$$

Note that we have added E_0 to the isentrope to reflect the heat of detonation of the unreacted explosive. Other choices are possible but this one is convenient in regards to application of the shock relations. The form of Γ is also modified. For the products there is a limit to the compression in a single shock, given by

$$y_{\max} = \frac{2}{\Gamma_p(y_{\max}) + 2} \quad (11)$$

Using the given function for $\Gamma(y)$ and the expression for the limit of y one can solve for y_{\max} and $\Gamma(y_{\max}) = \Gamma_{sc}$ where the subscript sc stands for shock compression limit. To make the shock compression limit for the reactants the same as the shock compression limit for the products $\Gamma_r(y)$ is defined to be

$$\Gamma_r(y) = \Gamma_r^0 + Z y \quad (12)$$

where $\Gamma_r^0 = \beta c^2 / C_p$ the thermodynamic definition, with β the thermal expansion coefficient, c the sound speed, and C_p the specific heat at constant pressure, and

$$Z = (\Gamma_{sc} - \Gamma_r^0) / y_{\max} \quad (13)$$

HUGONIOT CURVES FOR REACTANTS AND PRODUCTS

The Rankine-Hugoniot relations apply to both reactants and products throughout the reaction zone, under the assumptions stated earlier. For a plane, steady wave in the strong shock approximation where the shock speed is D is given as $D = u / y$, the pressure as $p = \rho_0 D u$, and the specific internal energy as $E = E_0 + (D y)^2 / 2$ where E_0 is the energy of detonation. Using the $E(p, v)$ equations of state given above with the RH conditions one finds

TABLE 1. EOS AND THERMAL PARAMETERS FOR PBX9404-9501

Calibration Input

D_{CJ} (m/sec)	p_{CJ} (Gpa)	ρ_0 (kg/m ³)	E_0 (MJ/Kg)
8790	35.7	1844	5.85

Reactant EOS parameters

A(km/sec)	B	C	Γ_r^0	Γ_{sc}	y_{max}	Z
2.339	2.737	0.5	0.786	0.781	0.7192	-0.00729

Product EOS Parameters

k	a	n	v_c (m ³ /kg)	p_c (Gpa)	b
1.3	0.8067	1.447	0.8727×10^{-3}	3.376	0.7

Thermal Parameters

	C_v (J/kg K)	R(J kg K)	T_c	T_{atm} (K)
Reactants	3125	265.5	n/a	273
Products	885	265.5	2295	273

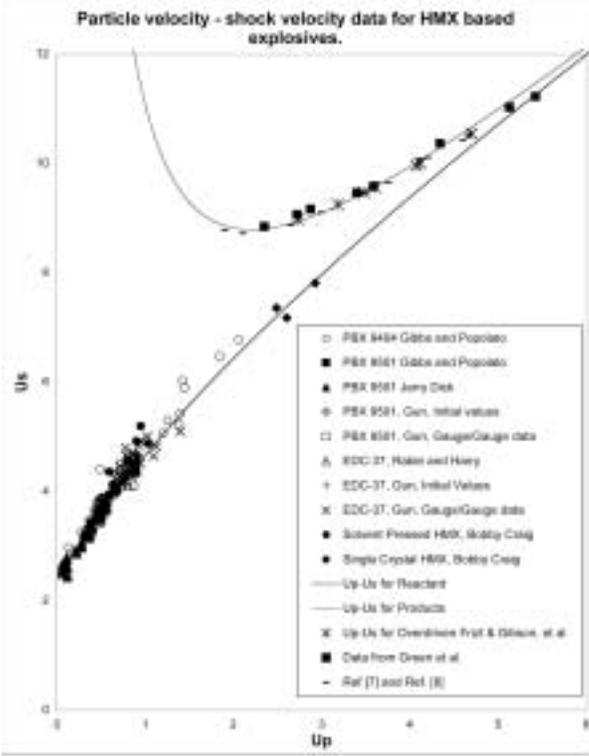


Figure 1. UP-US (or u-D) for the modified reactant EOS Compared against Gustavsen's compilation, [6] and Refs. [7] and [8] for HMX-based explosives

$$D_r^2 = \frac{2}{y} \cdot \frac{[(v/\Gamma_r)p_r^S - E_r^S]}{[(v/v_0)(2 + \Gamma_r)/\Gamma_r - 1]} \quad (14)$$

$$D_p^2 = \frac{2}{y} \cdot \frac{[(v/\Gamma_p)p_p^S - E_p^S]}{[(v/v_0)(2 + \Gamma_p)/\Gamma_p - 1]} \quad (15)$$

The apparent symmetry of these two expressions is deceptive. The shock speed of the reactants approaches the sound speed A as y goes to zero and then increases monotonically as y increases, while the shock speed of the products goes to infinity as y goes to zero, describing to the constant volume weak detonation. The shock speed of the products at first decreases as y increases, reaches a minimum at the CJ point, and then increases through the end states of strong detonations. A plot of shock speed versus particle speed for both the reactants and products is shown in Fig. 1. The figure displays a collection of experimental results for HMX-based explosives (PBX 9501-9404 and LX-17) according to different

researchers, as compiled by R. Gustavsen, [6] and Refs. [7] and [8]. Table 1 lists the values used to display all the figures in this paper.

The denominator vanishes at $v/v_0 = \Gamma/(2 + \Gamma)$ for both reactants and products, corresponding to the shock compression limit for a single shock, and the shock and particle speeds go to infinity there.

COMPLETE EOS FOR REACTANTS AND PRODUCTS

The EOS given above are of the form $E(p, v)$. They are incomplete EOS, as they describe only the mechanical properties and provide no information about the thermal properties, temperature and entropy. For the apportionment of energy between the reactants and the products, the thermal properties are needed.

Gruneisen gamma is defined by

$$\Gamma = -\frac{v}{T} \left(\frac{\partial T}{\partial v} \right)_S \quad (16)$$

and integrating it gives the temperature on the reference isentrope. For the reactants the temperature on the reference isentrope is

$$T = T_0 e^{-Z(1-v/v_0)} \left(\frac{v}{v_0} \right)^{-(\Gamma_r^0 + Z)} \quad (17)$$

For the products the temperature on the reference isentrope is given in [3] as

$$T_p^S(v) = T_c \frac{[\frac{1}{2}(v/v_c)^n + \frac{1}{2}(v/v_c)^{-n}]^{(a/n)(1-b)}}{(v/v_c)^{k-1+a(1-b)}} \quad (18)$$

Temperature off the reference isentrope is given, with the assumption that the specific heat at constant volume C_v is constant, by

$$T = T^S(v) + \frac{E - E^S(v)}{C_v} \quad (19)$$

The specific heat of the reactants is regarded as a value that can be chosen so that the shock temperature has a

plausible value, which for these calculations we set to 1600 degrees K.

The entropy is included by integrating the thermodynamic identity

$$\left(\frac{\partial E}{\partial S}\right)_v = T \quad (20)$$

using the expression above for T. The result is

$$E(S, v) = E^S(v) + C_v T^S(v) \left[\exp\left(\frac{S - S^*}{C_v}\right) - 1 \right] \quad (21)$$

where S^* is the value of entropy on the reference isentrope. Now S_r^* is just the specific entropy of the unreacted explosive in the initial state and it can be chosen to have any convenient value. S_p^* must have the same reference, but it has a different value. In principle, it can be referenced to S_r^* through careful application of the Fickett-Jacobs diagram [5] but in practice the reference is unknown. Fortunately all that is usually needed is the $S - S^*$ for either products or reactants. The usual system has the entropy changed by a shock wave, and in that case the energy $E(S, v)$ is known from the jump conditions, so that $S - S^*$ can be found from (21). Then the subsequent processes are usually isentropic, and $S - S^*$ remains constant. The family of isentropes can be found by using $(\partial E / \partial v)_S = -p$ and differentiating (21) with the substitution $(\partial T / \partial v)_S = -\Gamma T / v$ to get

$$p^{isentrope} = p^S(v) + \frac{\Gamma C_v T^S(v)}{v} \left[\exp\left(\frac{S - S^*}{C_v}\right) - 1 \right] \quad (22)$$

MIXTURE EOS, PERFECT MIXING AND CLOSURE ASSUMPTIONS

Here we discuss the hydrodynamic mixture equation of state, $E(p, v, \lambda)$. We assume perfect mixing of the

reactants and products. We also assume that there is pressure equilibrium between the phases so that $p = p_r = p_p$. The variable λ represents the mass fraction of products, $1 - \lambda$ is the mass fraction of the reactants. The specific volume and the specific internal energy are represented by the weighted sums

$$v = (1 - \lambda) v_r + \lambda v_p \quad \text{and} \quad E = (1 - \lambda) E_r(v_r, p_r) + \lambda E_p(v_p, p_p) \quad (23)$$

and pressure equilibrium is used assumption to replace p_r and p_p by the mixture pressure p . To carry out hydrodynamic analysis, given λ and v , we need to compute either E given p , or visa versa. We see that this representation introduces two additional quantities, v_r and v_p the phase volumes of the gas and solid.

An additional closure assumption is needed to reduce the dependence of the mixture energy to a single pressure and a single volume variable. Suppose for a moment, without justification, that it was deemed satisfactory to take the ratio reactant phase volume to that of the products

$$\Phi = \frac{v_r}{v_p} \quad (24)$$

and that Φ depended at most on λ and v . Then the mixture rule for volume (23a) and (24) are two linear equations for v_r and v_p with solutions

$$v_r = \frac{\Phi v}{\lambda + (1 - \lambda) \Phi}, \quad v_p = \frac{v}{\lambda + (1 - \lambda) \Phi} \quad (25)$$

With Φ known, the $E(p, v, \lambda)$ EOS is written as

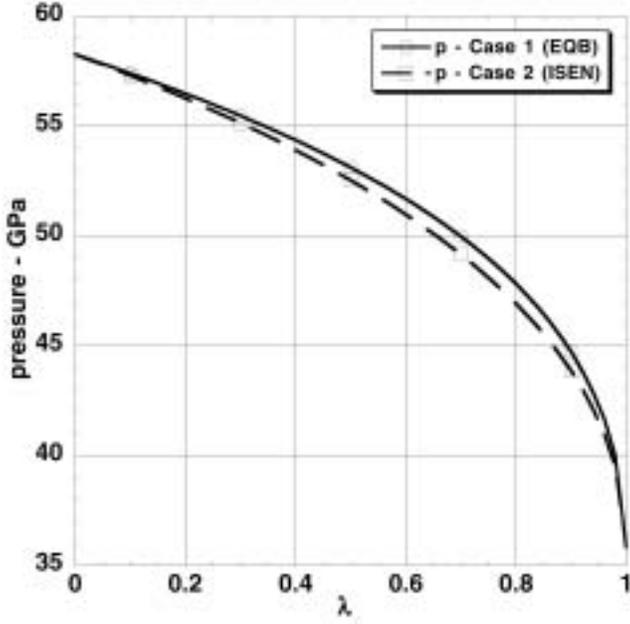


Figure 2. Plot of the pressure versus reaction progress for the two closures, pressure-temperature equilibrium, Case 1 and isentropic expansion of the solid (no heat transfer) Case 2.

$$E(p, v, \lambda) = \left(E_r^S(v_r) + \frac{v_r}{\Gamma_r(v_r)} [p - p_r^S(v_r)] \right) (1 - \lambda) + \left(E_p^S(v_p) + \frac{v_p}{\Gamma_p(v_p)} [p - p_p^S(v_p)] \right) \lambda \quad (26)$$

where the functions $p_r^S(v)$, $p_p^S(v)$, $E_r^S(v)$, $E_p^S(v)$, $\Gamma_r(v)$ and $\Gamma_p(v)$ are those defined previously.

CLOSURE MODELS

Pressure-Temperature Equilibrium and No Heat Transfer to the Reactants

In the preceding paragraph we assumed that ratio of the volume of the reactants to products $\Phi = v_r / v_p$ as known. It follows that (26) is a useable hydrodynamic equation of state. The exact form of this function is modeled by a closure condition that is to be used with our original assumption of pressure equilibrium between reactants and products, $p = p_p = p_r$. There are

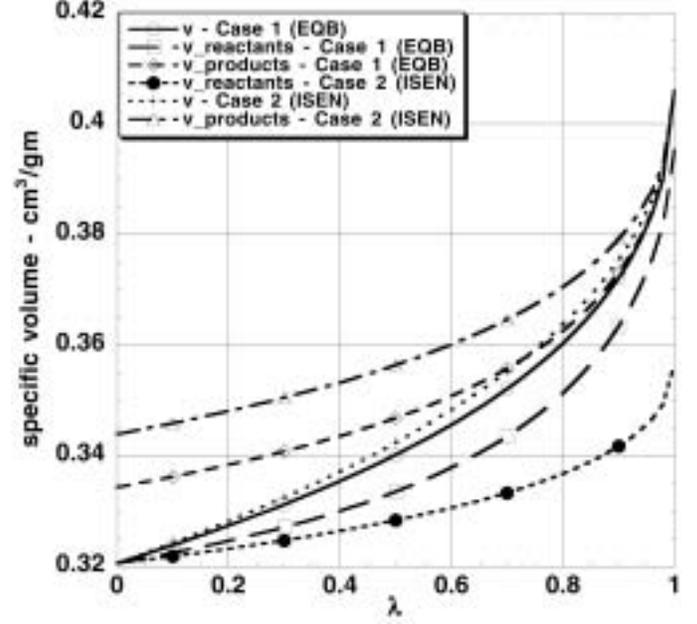


Figure 3. Plot of the specific volume versus reaction progress for Case 1 and Case 2.

two limiting cases that can be considered. Case 1 assumes that the reactants and the products are in thermal equilibrium. This is mostly likely to be strictly valid where the explosive is near complete reaction and hence towards the end of the reaction zone. The additional closure assumption is expressed as

$$T_r = T_p \quad (27)$$

Case 2 assumes that all the energy liberated in the reaction stays in the products; there is little or no time for transfer of heat to the reactants and subsequently behind the lead shock, the expansion of the reactants is isentropic. If the pressure on the p, v - isentrope is $p^{isentrope}(v)$, as defined by (21), say, then the no heat transfer closure is

$$p = p^{isentrope}(v) \quad (28)$$

Figures 2 - 7 show the reaction zone profiles for the two different closure assumptions, Case 1 (pressure, temperature equilibrium) according to (27) and Case 2

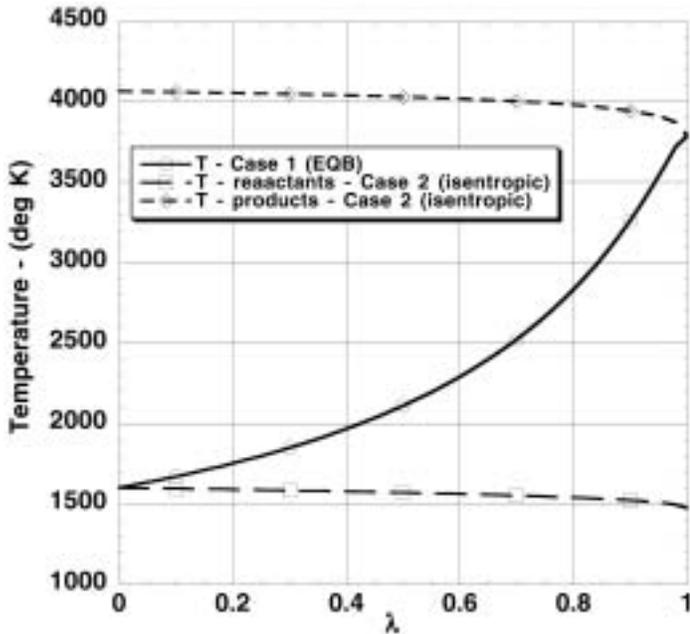


Figure 4. Plot of the temperature versus reaction progress for Case 1 and Case 2. Case 2 delineates between the reactant and gas phases.

(isentropic expansion of the reactant, or no heat transfer) according to (28). The main difference between the two cases is that Case 2 allows for different temperatures of the reactants and products, whereas Case 1 displays an equilibrium temperature that varies in the reaction zone between the von Neumann spike temperature of 1600 degrees K and the CJ temperature of 3786 degrees K. There is a temperature maximum in the profile very close to complete reaction that is not readily discernible in the Fig. 4. Another striking observation is that while there are significant variations in the specific volumes for the reactant and products between the two cases, see Figure 3, there is much less variation of the mechanical variables for the pressure, the mixture specific volume and the particle and sound speed. The mechanical states and therefore the hydrodynamic equation of state seem somewhat insensitive to the exact form of the closure, while the thermal states in the reaction zone are clearly sensitive to the form of closure.

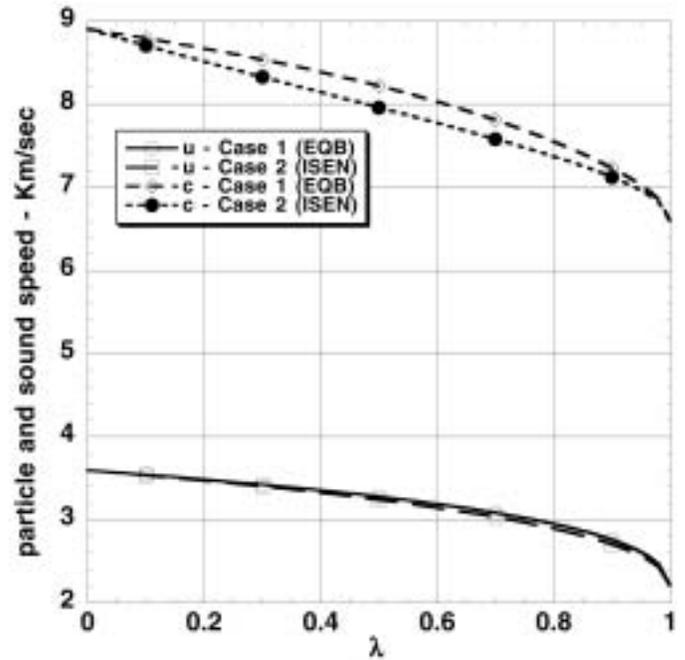


Figure 5. Plot of the particle and sound speed computed from the hydrodynamic EOS for Case 1 and 2.

Figure 6. shows the the ratio of the specific volume of the reactants to the products. The ratio ϕ is a function of λ for a CJ- detonation for both cases, and its value lies approximately in the range $0.88 \leq \phi \leq 0.98$. One observes that at least for the CJ case, that ϕ is nearly a constant. This observation is the basis for a simple closure model that is discussed in the next section. A similar plot of the ratio of the specific internal energies of the reactants to the products is shown in Figure 7, and unlike ϕ , this ratio has more variation.

SENSITIVITY AND A SIMPLE EXPLICIT MODEL

The results of the previous section suggest that the hydrodynamic equation of state is not extremely sensitive to the exact form of the closure. This assertion was tested by choosing different values of ϕ in the observed range, and two outlying values $\phi=0.88$ and $\phi=1.0$. A constant value of ϕ results in a closure model of the desired type that is linear in both E and p . And we found that if we chose a value well

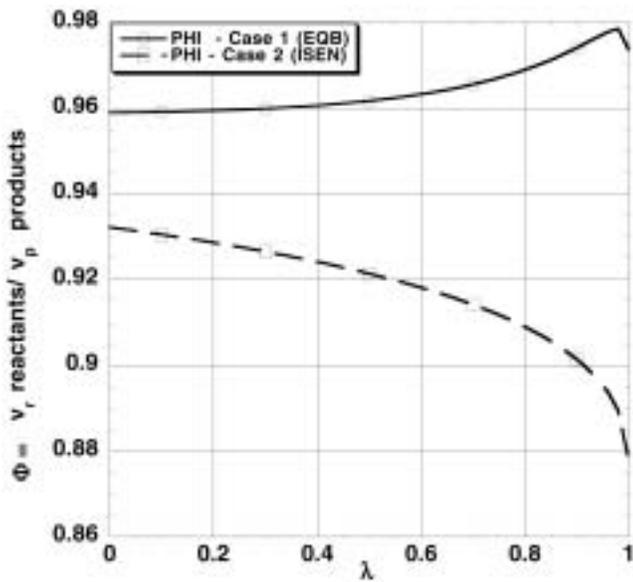


Figure 6. Plot of the ratio of the specific volume of the reactants to the product for Case 1 and 2. The volume ratio lies in a relatively narrow range.

within the range (for example, we display results for $\Phi = 0.94$), then the profiles for all the mechanical states for pressure, mixture specific volume, particle velocity and sound speed, were found to be intermediate and almost indistinguishable from the profiles of Case 1 and Case 2.

Figure 10 shows such a comparison for the pressure. However for values of Φ outside this range, then we started to see significant deviation. This same observation is reflected in Figs. 8 and 9 which show plots of the temperature of the reactants and products as a function of the reaction progress variable for Case 1 and 2 and the values of constant Φ . Figure 10 shows the corresponding temperature profiles. For values inside the range $0.88 \leq \Phi \leq 0.98$, the temperature in both the reactants and products stays in a plausible range between 1600 and 10,000 degrees K. While outside the range the temperature is extremely high or even negative (an artifact of the thermal modeling). In either case the temperature profile is not plausible. This suggests a simple closure model that uses of Φ constant requires that

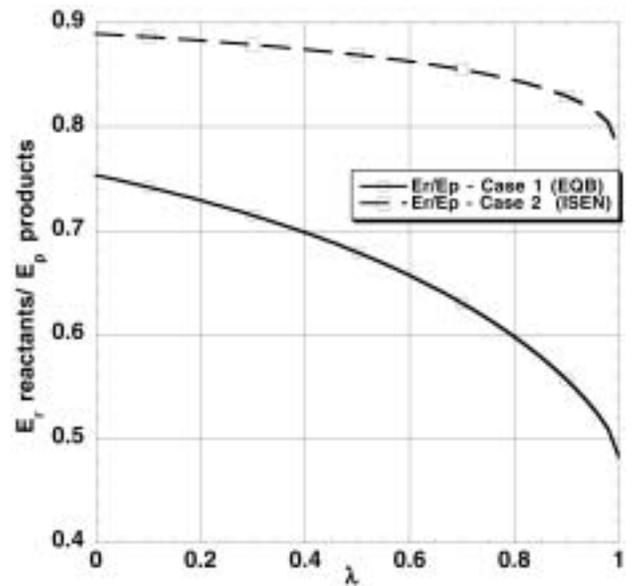


Figure 7. Plot of the ratio of the specific internal energies of the reactants to products for Case 1 and 2. The energy ratio has more variation than the specific volume ratio.

its value be in a range constrained by reasonable thermal profiles. Figures 6, 8 and 9 clearly show that one could pick out other temperature paths $T(\lambda)$ by choosing $\Phi(\lambda)$ properly. For example by looking at Fig. 6, one could choose to start out with no heat transfer to the reactants and go smoothly to thermal equilibrium near the CJ value; hence other tractable modeling choices are possible other than constant Φ .

CONCLUSIONS

An equation of state whose limiting form for both reactant and products, fit available experimental data and can be used in the hydrodynamical modeling of the detonation reaction zone, can be constructed using simple mixture theory and simple closure models. The simplest closure we considered here assumes that the ratio of the specific volumes of the reactants to the products is a constant. However consideration of the thermal properties of the mixture require that this ratio be chosen to be in a narrow range that reflects plausible reaction zone temperatures.

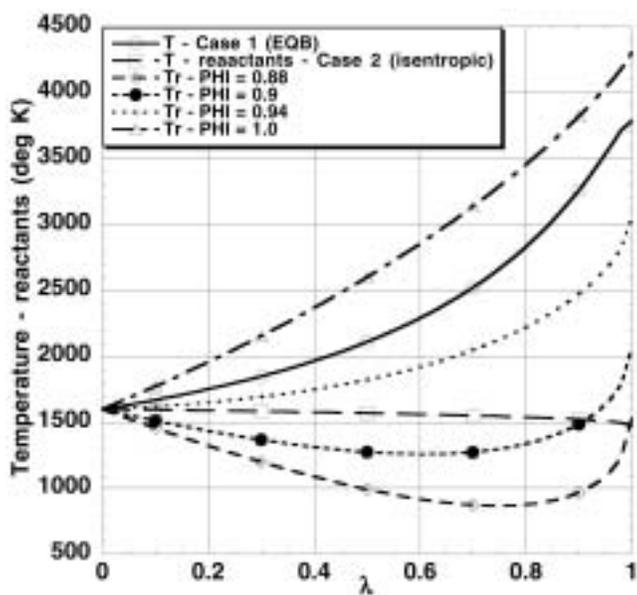


Figure 8. Plot of the temperature of the reactants versus reaction progress different closures, Case 1 and Case 2 and different constant values of ϕ .

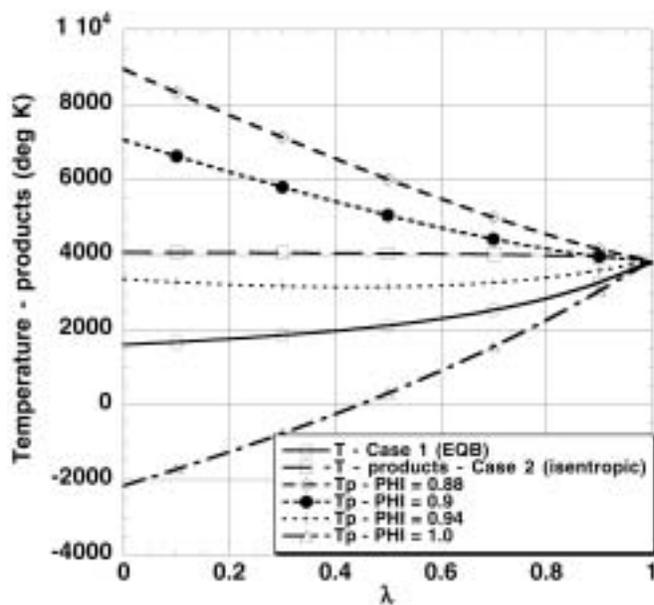


Figure 9. Plot of the temperature of the products versus reaction progress different closures, Case 1 and Case 2 and different constant values of ϕ .

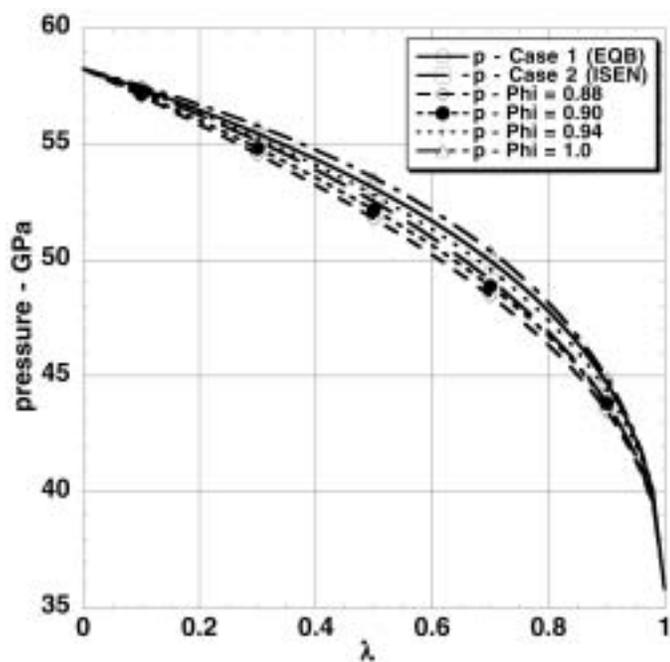


Figure 10. Plot of the pressure as a function of reaction progress variable for different closures, Case 1 and Case 2 and different constant values of ϕ .

Clearly if one has temperature sensitive reaction rates then more careful consideration must be made to the specific form of the closure. If instead one has mechanically dependent rates, i.e. dependent on the specific volume and or pressure, perhaps the form of the closure is not terribly sensitive and one can get by with a simple model that choses the ratio of the specific volumes of the reactants and products to be constant (say) and it may be adequate over broad range of conditions. More work is required to test this EOS model for dynamic cases and the intended application to ignition and multidimensional detonation.

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