THERMODYNAMIC REPRESENTATIONS FOR SOLID PRODUCTS IN IDEAL DETONATION PREDICTIONS

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There are a number of established computer programs for the prediction of the ideal detonation characteristics of condensed phase energetic materials. These basically comprise thermochemical computer codes consisting of a chemical equilibrium solver for a number of phases having different equations of state (EoS), providing predictions of Chapman Jouguet and related detonation conditions. Many of these now employ sophisticated, intermolecular potential based EoS for fluid products but normally rely on very simple representations for solid and melt phase products and inert explosive components. The basic requirements of any solid EoS for these calculations are
- the EoS should be a good representation of experimental Pressure-Volume-Temperature-Energy data and associated derivatives of these quantities for the particular phase and should be a thermodynamically complete EoS
- the predicted thermodynamic parameters for a given phase should be in analytic form and without discontinuities
- the EoS should contain parameters that are readily measurable and the number of parameters should be in accord with available experimental or theoretical data
- the EoS should not carry an excessive computational cost
In recent years the Vinet "universal" EoS has been modified and extended to enable the description of solid and melt phases for condensed phase detonation product species, both ionic and covalent. Solid products in both commercial explosives and insensitive heterogeneous munitions can have a significant effect on the detonation characteristics and associated isentropic expansions, because of the form of the solid/melt EoS. A number of solids EoS have been incorporated into a modern ideal detonation computer code and the paper will compare detonation characteristics for a typical explosive. The application of this EoS to the description of the unreacted Hugoniot of a multi-phase explosive and predictions of shock temperatures will also be discussed.

INTRODUCTION

Mathematical simulations of explosion and detonation processes require descriptions of the mechanical, thermal and chemical kinetic regimes that govern these events. A variety of Equations of State (EoS) have been used to describe both unreacted explosives and their reaction products. These have ranged in complexity from full statistical mechanical intermolecular potential based EoS for fluids to lumped chemistry implicit relationships describing principal product isentropes.

From a thermodynamic perspective, condensed phase detonation modelling can be divided into the following categories:

- (i) ideal detonation/ thermochemical calculations
- (ii) approximate non-ideal detonations e. g. ZND, slightly divergent flow, DSD (1 & 2-D)
- (iii) full numerical detonation simulations e.g. hydrocodes.

IDEAL DETONATION CODES - EoS

Modern ideal detonation codes[1,2,3] employ full (Energy-E, Pressure-P, Volume-V, Temperature-T) thermodynamic EoS and are no longer reliant on approximate empirical or semi-empirical fluid chemistry explicit forms with their associated uncertainties and need for re-parameterisations. The intermolecular repulsive forces in the detonation product fluid molecules largely govern detonation behaviour in explosives. There remain some uncertainties in inter-species mixing rules and the effect of pressure on intramolecular force contributions.

In CHNO explosives with an appreciable oxygen balance deficit and in energetic media containing species with other elements, solid products can also be produced. In the context of ideal detonation (1-D process leading to a chemical /mechanical /thermal equilibrium state) the finite rate "clustering" processes involved in the formation of solid media is ignored.

Ideal detonation predictions are well known to be less sensitive to the thermodynamics of the solid or melt phases than the fluid phase products. Simple EoS, some with a PV only relationship and a temperature dependent heat capacity representation, have found to be satisfactory in most circumstances for high explosives[1,2]. In some energetic media, notably commercial explosives, high solids product loadings are possible and there is a need to include solids EoS with thermal expansion component. In some instances Hugoniot data will not be available for the solid phases concerned and an EoS based on published material properties is preferred.

NON-IDEAL DETONATION CODES – EoS

Non-ideal detonation modelling involves finite rate chemistry and, with the exception of 1-D dimensional studies (planar shocks), shock hydrodynamic equations. In ZND[4] theory and some slightly divergent flow simulations it is sometimes possible to include the full thermodynamics of an ideal detonation code for the product molecules[3]. Simple, often phenomenological, EoS are used to describe the unreacted explosive[5]. The use of an explicit PVT EoS in these circumstances is rare, largely because the lumped chemical rate expressions currently avoid the formal use of temperature or entropy.

NUMERICAL SIMULATIONS OF DETONATIONS

In hydrocode modelling, the use of complete thermodynamic chemistry explicit EoS would be prohibitively expensive in terms of processor time. Much hydrocode modelling is based on thermodynamics (reactant and products) and chemical rate expressions formulated in terms of energy, pressure and volume only. For some applications the behaviour of the explosive is better described in terms of constitutive relations. Where a more detailed study is required it is likely that temperature dependent chemical reaction rate will be required and a universal EoS will have applications. However, for some applications the behaviour of the explosive will be better described in terms of constitutive relations.

HIGH TEMPERATURE AND PRESSURE SOLIDS EoS

A number of thermodynamic EoS for solids has been used in condensed phase explosion simulations. In most cases the temperature dependent heat capacity is introduced separately in a polynomial, Einstein or Debye form. The additional PVT expressions are briefly reviewed here
.

COWAN EoS

Though incompressibility is a reasonable approximation for some high explosives, the Cowan EoS[6] has been used for graphite in some early detonation computer codes. The pressure, P, is given as

$$P = p_1(\eta) + a(\eta) + b(\eta)T^2 \qquad (1)$$

where $p1$, a and b are polynomials in the compressibility η. This EoS requires many parameters and is not considered further in this paper for this reason.

MURNAGHAN EoS

The Murnaghan EoS[7] has a simple form, requiring few parameters it is usually given as (MURN)

$$V = V_0(1 + B_0'P/B_0)^{-1/B_0'} \qquad (2)$$

where V, B_0 and B_0' are the volume, bulk modulus and bulk modulus pressure derivative respectively with the subscript 0 denoting ambient conditions.

An extended form of the Murnaghan EoS[3] including thermal expansion term is included in Cheetah (MURNE) –

$$V = V_0(\exp\{-\alpha_0(T - T_0) + B_0'P/B_0)^{-1/B_0'} \qquad (3)$$

where α_0 and T define thermal expansion coefficient and temperature.

VINET EOS

A universal EoS for solids was developed by Vinet et al[8]. This can be applied to a broad range of condensed phase media over a wide range of temperature and pressure. As with the Murnaghan EoS it requires few parameters and has the form (VINET)

$$P = \frac{3B_0(1-\eta)}{\eta^2}\exp[\frac{3}{2}(B_0' - 1)(1-\eta)]$$
$$+\alpha_0 B_0(T - T_0) \qquad (4)$$

This approach assumes that the $\alpha_0 B_0$ term is constant above the Debye temperature and volume invariant. We have previously extended this EoS[9] by assuming a simple cubic polynomial for $\alpha_0 B_0$ below this temperature: this has been found to work well down to temperatures of ¼ of the Debye value for a wide variety of different solids.

PARSAFAR MASON EOS

An approach similar to Vinet was taken by Powell et al[10] and extended[11] to include a thermal pressure coefficient, θ. In this EoS (PMV), the pressure is given as

$$P = P_0 + b_2\eta^{-2} + b_3\eta^{-3} + b_4\eta^{-4}$$
$$+\theta(T - T_0)$$
(5)

In the original formulation b_2, b_3 and b_4 were temperature dependent: more recent work and this study have assumed they are temperature invariant, considerably simplifying the EoS. Some computational advantage over the Vinet EoS might be obtained from integer powers in this expression though obtaining the additional parameter might be problematic.

SOLID EOS – HUGONIOT FITS

In a comparative study, Hugoniot data[12] for graphite (pyrolytic) and alumina have been used and EoS parameters and Hugoniot temperatures obtained by non-linear regression. Data for diamond are taken from van Thiel and Ree[13].

The thermal expansion coefficients were kept constant for all EoS: this was both for consistency, and the apparent weak dependence of the fit to this parameter. Heat capacity data at constant pressure were taken from standard sources and converted to constant volume heat capacities, C_V. The resultant data were represented by the polynomial

$$C_V = C_{V1} + \frac{C_{V2}}{T} + \frac{C_{V3}}{T^2} + \frac{C_{V4}}{T^3}$$
(6)

Parameters uses in these calculations are listed in Table 1: numbers in brackets refer to power of 10 exponents. SI units are used throughout and the molar volume quoted, Vo, is an average of Hugoniot sample densities used. It can be seen that similar bulk moduli and their pressure derivatives are found using different EoS.

TABLE 1. EoS DATA FOR GRAPHITE AND ALUMINA

	Graphite	Alumina
α	2.3(-5)	5.5(-6)
B_{0MURN}	4.298(10)	3.135(11)
$B_0'_{MURN}$	5.298	2.50
B_{0MURNE}	4.273(10)	3.138(11)
$B_0'_{MURNE}$	5.193	2.472
B_{0VINET}	4.0(10)	3.122(11)
$B_0'_{VINET}$	6.663	2.639
b_2	-7.833 (10)	-4.525(11)
b_3	9.282(10)	6.323(11)
b_4	-1.629(10)	-1.781(11)
θ	1.303(6)	1.538(6)
C_{V1}	2.434(1)	1.4833(2)
C_{V2}	-1.108(3)	-2.892(4)
C_{V3}	3.085(6)	5.934(6)
C_{V4}	5.994(8)	-1.045(9)
$S^0_{289\,K}$	5.686	50.92
$\Delta H^0_{298\,K}$ kJ/mol	0	-1675.7
Vo m^3/mol	5.452(-6)	2.564(-5)

The standard of fits for the two sets of Hugoniot data were similar. A fit for alumina using the Vinet EoS is illustrated in Figure 1.
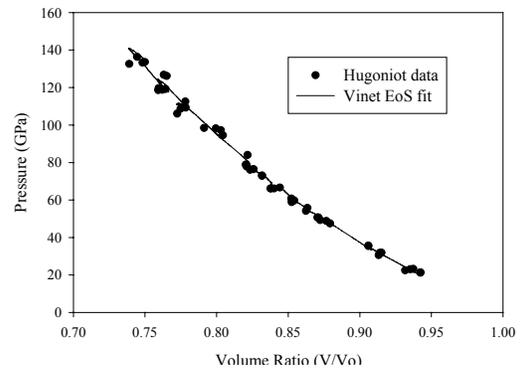

FIGURE 1. HUGONIOT DATA AND VINET EoS FIT FOR ALUMINA

A comparison of different Hugoniot temperature predictions is shown is Figure 2. Here the temperature plots have been smoothed.
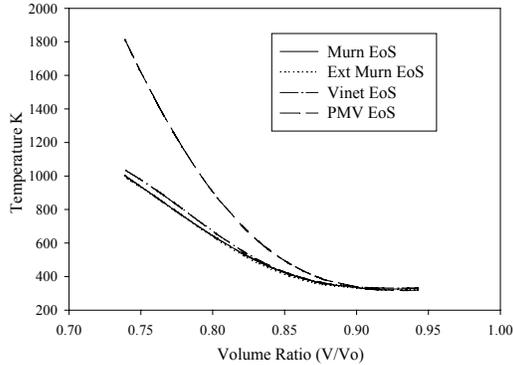

FIGURE 2. PREDICTED SHOCK TEMPERATURES FOR ALUMINA

The shock temperatures predicted by the different EoS for alumina are similar with the exception of the PMV EoS.

A set of plots for graphite are illustrated in Figures 2 and 3. Here the temperature predictions are similar and there is clear evidence of a phase change occurring at high pressure.
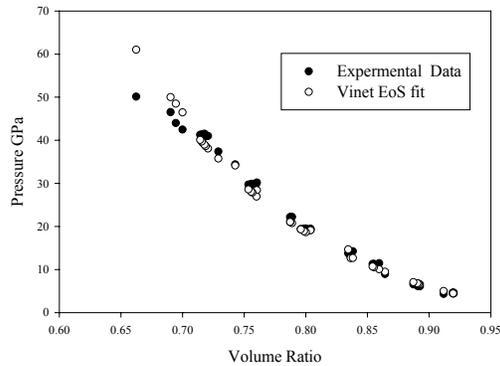

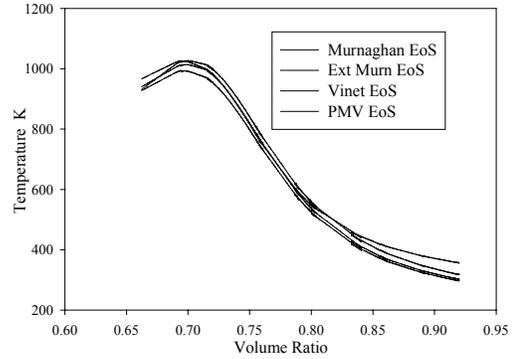**FIGURE 3: HUGONIOT DATA AND VINET EoS FIT FOR GRAPHITE**

FIGURE 4. PREDICTED SHOCK TEMPERATURES FOR GRAPHITE

GRAPHITE-DIAMOND PHASE DIAGRAM

A sterner test of EoS is to compare predictions of phase transition temperatures at different pressures. Three EoS have been used with parameters from van Thiel and Ree[13] for the species at their theoretical maximum density in a comparison of graphite-diamond phase transition temperatures: also included are experimental data. Given the simple nature of equation (4) the agreement with experiment for phase transitions is very good in comparison to the Murnaghan and extended Murnaghan EoS..
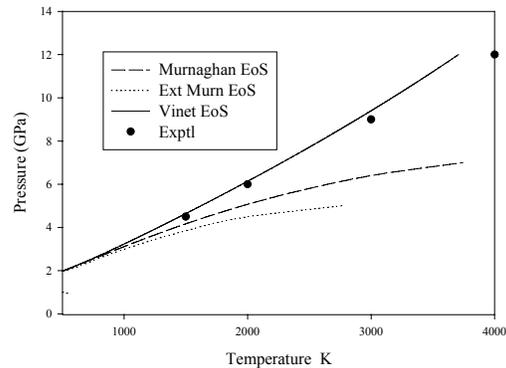

FIGURE 5: CARBON PHASE DIAGRAM

PHASE TRANSITIONS AND THE APPROXIMATE MELT EoS FOR DIOPSIDE

Due to the high temperatures that prevail in a detonation it is necessary to include possible solid-melt phase transitions for products such as alkali halides and oxides.

As an example, we have studied diopside, $CaMgSi_2O_6$ for which a full set of experimental data exist (Table 2).

Figure 6 illustrates a comparison of predicted $P-V-T$ data for both the melt and solid phases of diopside and experimental Hugoniot data[14]. Agreement between experiment and prediction is good. The variation in volume as a function of temperatures for a range of pressures is shown in Figure 3. The clear increase in molar volume upon melting of about 20% is in good agreement with experiment as is the effect of pressure on melting point of approximately 180 K GPa^{-1}.

TABLE 2: VINET EOS - INPUT PARAMETERS FOR DIOPSIDE

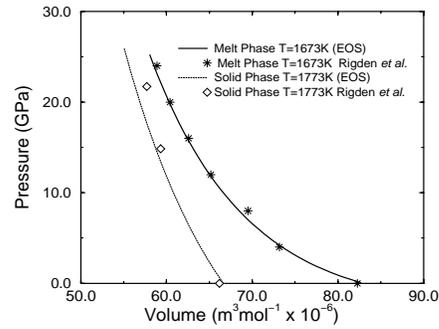| Diopside	Solid	Melt
T_R	1664	1664
α	3.2(-6)	6(-6)
B_0	9.07(10)	2.19(10)
B'_0	4.5	6.9
V_0 $m^3\,mol^{-1}$	69.11 (-6)	82.95 (-6)
U_0 $kJ\,mol^{-1}$	-3206.2	-2656.5
S_0 $J\,(K\,mol)^{-1}$	142.9	619.8

FIGURE 6. EOS OF SOLID AND MOLTEN DIOPSODE AT 1663 AND 1773 K

As a final validation the Gibbs energies of both the solid and melt phases of diopside are plotted along with experimental data[14] over a range of temperature in Figure 7. Agreement is excellent and the comparison comprises a stern test of the model given the several thermodynamic quantities involved.
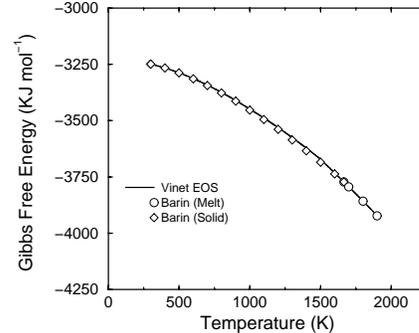

FIGURE 7. VARIATION OF GIBBS FREE ENERGY FOR DIOPSIDE

IDEAL DETONATION CODE – EFFECT OF SOLID EoS

An ideal detonation computer code was run with four different EoS for a generic explosive (80 % w/w TNT and 20% w/w aluminium) at a density of 1500 kg/m^3. The computer program used an intermolecular based fluid EoS, allowing for CO, CO_2, CH_4, H_2, N_2, O_2, N_2, H_2O, and NH_3 as fluid products. Solid products

included graphite, diamond and alumina. The code is discussed in detail elsewhere[1,15].

Values for the ideal detonation conditions and the CJ isentrope slope, Γ, are given in Table 3. The CJ state was close to the graphite-diamond phase transition and this is reflected in the variability of the isentrope slope. Graphite production is given (g.atoms/kg)

TABLE 3. IDEAL DETONATION CHARACTERISTICS – CHAPMAN JOUGUET STATE

	MURN	MURNE	VINET	PMV
VOD	5362	5587	5782	5693
P GPa	11.1	11.7	11.5	12.1
T	4826	4878	5202	4915
ρ	2020	2000	11960	2000
Γ	2.870	3.000	3.265	3.000
C(g)	14.60	10.0	15.0	12.5

EoS OF AN UNREACTED COMPOSITE EXPLOSIVE

Shocked composite media pose a considerable challenge to those working in the fields of thermodynamics and constitutive relations of shocked media. Neglecting the constitutive relation aspects, the simplest analysis of the effect of a shock on multiphase inert system assumes that –
  (i)   the media is in mechanical equilibrium
  (ii) either thermal equilibrium or more likely thermal isolation, are attained
  (iii) there is thermal equilibrium within each phase
  (iv) mechanical effects, such as friction or structural damage are ignored

With the above assumptions it is straightforward to apply conservation relations and equations of state to determine the shock Hugoniots of mixtures from data on individual immiscible components. For a plastic bonded explosive, X, consisting of a pure explosive, A, and a binder B, it can be shown that

$$Up^2{}_X = m_A Up^2{}_A + m_B Up^2{}_B \qquad (7)$$

where Up and m correspond to the particle velocity and mass fraction of the explosive and its constituents.

Figure 8 shows the above equation plotted for a PBX explosive (85 %w/w RDX. 20 %w/w HTPB binder)[16]. Hugoniot data for RDX has been plotted from the relation given by Dobratz[17]. Other data are taken from Bourne et al[16]. It can be seen the relation does not hold above 1 GPa.
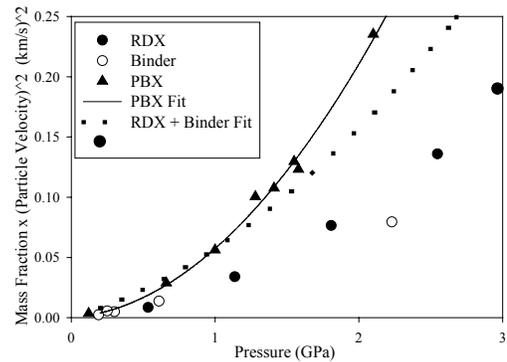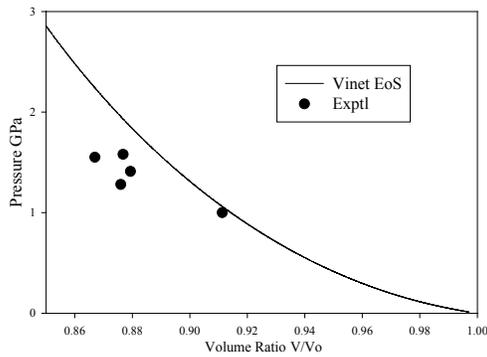

FIGURE 8. PARTICLE VELOCITY PLOT FOR PBX EXPLOSIVE AND ITS CONSTITUENTS

Shock Hugoniots for the two explosive ingredients were fitted to the Vinet EoS. A Debye heat capacity model was used for each ingredient. Figure 9 is the resulting shock Hugoniot plot comparing prediction

FIGURE 9. SHOCK HUGONIOT FOR PBX (RDX/HPTB) EXPLOSIVE

With measurement for the composite explosive with the two phases thermally isolated i.e. with the polymer phase reaching a much higher temperature. It is clear from this plot that the EoS overestimates the PBX explosive shock pressure and the reasons for this follow from Figure 8. The assumptions made at the outset do not hold: agreement is poorer still for the case of thermal equilibrium.

CONCLUSION

The Vinet EoS offers a simple and reliable solid and melt EoS for describing the thermodynamic properties of solid and melt phases in condensed phase explosion problems. It has the advantage that data for it (bulk modulus and its pressure derivative and thermal expansion coefficient) are likely to be available in the open literature.

The choice and parameterisation of a solids EoS in ideal detonation predictions can make a substantial difference in systems with heavy solid product loading or those containing significant quantities of inert materials. The difference can become amplified, in terms of the isentrope slope, near a solid phase transition.

The shock properties of polymer containing composites cannot be described in terms of thermodynamic EoS alone.

ACKNOWLEDGEMENTS

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