Williamsburg Equation of State for Modelling Non-Ideal Detonation

W. Byers Brown, Z. Feng, M. Braithwaite

► To cite this version:

W. Byers Brown, Z. Feng, M. Braithwaite. Williamsburg Equation of State for Modelling Non-Ideal Detonation. Journal de Physique IV Proceedings, 1995, 05 (C4), pp.C4-209-C4-214. 10.1051/jp4:1995418 . jpa-00253717

HAL Id: jpa-00253717

<https://hal.science/jpa-00253717>

Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Williamsburg Equation of State for Modelling Non-Ideal Detonation

W. Byers Brown, Z. Feng* and M. Braithwaite**

Mass Action Research Consultancy, Devonshire House, 14 Corbar Road, Buxton SK17 6RQ, U.K.

** Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.*

*** ICI plc Explosives GTC, Ardeer Site, Stevenston, Ayrshire KA20 3LN, Scotland, U.K.*

ABSTRACT

The recently developed Williamsburg equation of state (EOS) for detonation products is used in the one-dimensional ZND model for the reaction zone of a condensed explosive. This appears to be the first time a realistic EOS, capable of describing entropy and temperature changes accurately, has been incorporated into the ZND model. The unreacted explosive is described by a new Parsafar-Mason-Vinet EOS so that both phases receive the best thermodynamic treatment currently available. Results for the two extreme inter-phase assumptions regarding the thermal interaction of the reactant and product phases are presented and discussed.

1. INTRODUCTION

The thermodynamic behaviour and interaction of the reactant explosive and its products within the reaction zone are of crucial importance to the detailed structure of a detonation wave, and to its propagation. The reacting material within the reaction zone should therefore be described by realistic thermodynamics. The traditional assumption is that the reacting material can be regarded as a mixture of two phases, one consisting of the as yet unreacted explosive and the other of the detonation products. The problem of the thermodynamics of the reacting material is thereby simplified into finding appropriate equations of state (EOS) for the separate phases.

Early treatments used the polytropic equation for both unreacted explosive and detonation product gases, often with the same polytropic index. This EOS is unsuitable for liquids and solids, and is not in agreement with experiment. The Jones-Wilkins-Lee (JWL) EOS is much more flexible, but assumes the Grüneisen gamma coefficient is constant, and is not a complete equation of state, so that temperature and entropy cannot be calculated without a subsidiary crude assumption, for example that the heat capacity is a constant, which is never true.

The new WILLIAMSBURG (WBG) EOS for detonation products, proposed by Byers Brown and Braithwaite [1,2,3,4,5], is unusual in giving the specific energy E as a function of the specific volume V and the specific entropy S , and is therefore a complete EOS, embracing both mechanical and thermal properties, particularly well suited for describing adiabats and shocks. The comparatively small number of parameters it involves can be found by fitting the principal adiabat calculated from an ideal detonation code, for example IDEX [6], incorporating a sophisticated EOS based on statistical mechanics and intermolecular potentials. The WBG fits of energy, pressure, temperature, adiabatic and Grüneisen gammas and heat capacity, are highly satisfactory for a wide range of explosives.

In this paper we solve the one dimensional conservation equations for the Zeldovich-von Neumann-Döring (ZND) steady state of the reaction zone as a function of the extent of reaction parameter λ , with the WBG and (where possible) the JWL EOSs for the detonation products, and a new EOS (dubbed PMV) combining features of the recently proposed Parsafar-Mason [7] and Vinet [8,9,10] EOSs to describe the unreacted explosive.

The inter-phase condition determining the thermal interaction between the reactant and products, and the increase of entropy in the reaction zone, are especially featured and discussed.

2. ZND MODEL

We start from the basic one-dimensional conservation equations [11] and the reactive EOS,

$$P - P_0 = (\rho_0 D)^2 (V_0 - V) \quad (\text{Rayleigh line}), \quad (2.1)$$

$$E - E_0 = \frac{1}{2} (P + P_0) (V_0 - V) \quad (\text{Rankine-Hugoniot}), \quad (2.1)$$

$$P = f(E, V, \lambda) \quad (\text{reactive EOS}), \quad (2.3)$$

where $\rho = 1/V$ is the density, D the detonation speed, P the pressure, E the specific energy, and the zero subscript indicates the initial state. For a given value of D , provided the EOS relations are given, the equations can be solved numerically. In our paper, standard NAG (Numerical Algorithms Group) Library subroutines are employed to solve them.

3. EOS IN REACTION ZONE

Typically, the reacting material in the reaction zone is taken to be an ideal mixture of unreacted explosive and reacted product. Therefore their EOS determine the overall reactive EOS in the reaction zone according to an assumed mixing rule and the inter-phase conditions. The EOSs which are used in the calculations are as follows.

3.1 EOS for unreacted explosive

The PMV EOS [6] is a complete EOS, best defined in terms of Helmholtz free energy $A(T, V)$, which can be deduced from the following equations for the pressure

$$P = (\rho/\rho_0)^2 p_2 + (\rho/\rho_0)^3 p_3 + (\rho/\rho_0)^4 p_4 + \theta T, \quad (3.1.1)$$

and the specific heat capacity at constant volume,

$$C_v = C_\infty + C_1(T_0/T) + C_2(T_0/T)^2, \quad (3.1.2)$$

where the p_i , C_i , and θ (the thermal pressure coefficient) are constants. This basic form can be extended by the addition of further terms as required by the experimental data available.

3.2 EOS for reaction products

(a) WILLIAMSBURG (WBG)

This is a complete EOS with variables V , S which can be written in the simple form

$$E = \frac{PV}{g(v, \sigma) - 1}, \quad (3.2.1)$$

with

$$g(v, \sigma) = \gamma_0 + \sum_{j=1}^M \frac{\gamma_j}{1 + \beta_j v \sigma^{\alpha_j}}, \quad (3.2.2)$$

where $v = V/V_0$ is the reduced volume and σ is a reduced entropy factor defined by

$$\sigma = \exp[(S - S_0)/nR], \quad (3.2.3)$$

with n the moles per unit mass, R the gas constant, and

$$\overline{\alpha_j} = \alpha_j + \delta_j \log \sigma, \quad (3.2.4)$$

$$\gamma_0 = 1 + \sum_{j=1}^M \alpha_j \gamma_j, \quad (3.2.5)$$

where α_j , β_j , γ_j , δ_j are constants, and usually the number of terms for an adequate fit is $M=2$.

(b) JONES-WILKINS-LEE (JWL)

This is an incomplete EOS which can be written either in the form $P=P(E,V)$ or alternatively as

$$E = \frac{PV}{\gamma - 1} + \sum_{j=1}^M e_j \left(1 - \frac{\alpha_j v}{\gamma - 1} \right) \exp(-\alpha_j v), \quad (3.2.6)$$

where again $v = V/V_0$, and α_j , e_j , γ are constants, and usually $M = 2$, although here also the equation has been extended to a larger number of terms. It is postulated to be valid over the whole PV-plane. The familiar JWL equation for the pressure along an isentrope can be recovered by integrating the adiabatic differential equation $dE + PdV = 0$.

4. MIXING RULE AND INTER-PHASE CONDITIONS

4.1 Mixing Rule

As in the usual treatments, a linear phase mixing rule is assumed for all extensive properties, so that

$$V = (1 - \lambda)V_x + \lambda V_g, \quad (4.1.1)$$

$$E = (1 - \lambda)E_x + \lambda E_g, \quad (4.1.2)$$

where x and g denote the explosive and the gaseous products.

4.2 Inter-phase Conditions

To solve the equations, two further assumptions are needed to relate the two phases, which we call the inter-phase conditions. The first condition, as usual, is mechanical equilibrium:

$$P = P_x = P_g. \quad (4.2.1)$$

There are two alternative assumptions which lead to simple second inter-phase conditions.

(a) Thermal equilibrium:

$$T = T_x = T_g. \quad (4.2.2)$$

(b) Thermal isolation of the explosive phase:

$$S_x = \text{const.} \quad (4.2.3)$$

The two inter-phase conditions (a) and (b) are extreme cases. The first one indicates that the rate of heat conduction is infinite so that the two phases are always in thermal equilibrium. The second indicates there is no heat conduction between the unreacted explosive and the reaction products. Clearly, the actual situation will be somewhere in between these two extremes.

5. CALCULATION AND RESULTS

We use an ANFO explosive consisting of ammonium nitrate with 6% of a hydrocarbon ($\rho_0 = 0.85$ g/cc) as an example. The end-point of the reaction zone in ZND theory is the Chapman-Jouguet (CJ) state ($\lambda=1$), which according to the IDeX ideal detonation code [6] for this explosive has pressure $P_{CJ}=5.60$ GPa, specific volume $V_{CJ}=0.864$ cc/g, and detonation speed $D=5.02$ km/s. The WBG EOS for the products is constrained to have exactly the same CJ state, and the remaining parameters are fitted by a least squares procedure to the IDeX principal adiabat.

The PMV EOS for the unreacted explosive is fitted to experimental shock and thermodynamic results for ammonium nitrate modified to allow for the presence of 6% of a hydrocarbon of known density. The starting-point of the reaction zone in ZND theory is the von Neumann spike, which is at the intersection of the unreacted Rankine-Hugoniot ($\lambda=0$), calculated from the PMV EOS, and the Rayleigh Line through the initial and CJ states, which depends only on the product WBG EOS. The von Neumann pressure is $P_n=12.3$ GPa and the specific volume is $V_n=0.497$ cc/g. The results of the calculations on the PV-plane are shown in Figs 1 and 2.

Fig 1 PV-diagram for ZND detonation of ANFO assuming thermal equilibrium.

Fig 2 PV-diagram for ZND detonation of ANFO assuming thermal isolation.

Fig 1 is based on the assumption of thermal equilibrium between the explosive and product phases. The Rankine-Hugoniot of the unreacted explosive (described by the PMV EOS) is shown, ending at the von Neumann spike (VN), and also the straight Rayleigh Line between VN and the Chapman-Jouguet point (CJ). Also plotted, to the best of our knowledge for the first time, are the specific volumes of the individual explosive and product phases.

Fig2 is based on the assumption of the thermal isolation of the unreacted explosive phase, so the specific volume curve for the explosive is the adiabatic expansion from the Neumann point VN. It can be seen that the specific volume of the product phase is very close to the principal adiabat of the products which passes through the CJ point, so that unlike the thermal equilibrium case, very little additional entropy is created by the pre-CJ expansion.

It is not possible to use the JWL EOS for the gaseous products with the assumption of thermal equilibrium, since temperature is not defined. However, it can be used assuming thermal isolation of the explosive. It turns out that with JWL parameters chosen to make the CJ point agree exactly with that of the IDeX code (and therefore with that of the WBG EOS), there is no appreciable difference between the JWL and WBG individual specific volume curves.

Fig 3 $P\lambda$ -plot for ZND detonation of ANFO.

The WBG EOS is used for the products in all the calculations on which the subsequent figures are based. The $P-\lambda$ curves for the two assumptions are shown in Fig 3, and lie close together. Of greater interest and novelty, the specific volumes V_x and V_g , and also the total

Fig 4 $V\lambda$ -plots for ZND detonation of ANFO assuming thermal equilibrium.

Fig 5 $V\lambda$ -plots for ZND detonation of ANFO assuming thermal isolation.

specific volume V , are shown as functions of the extent of reaction parameter λ in Figs 4 and 5 for the two alternative interphase assumptions. Qualitatively they are similar, but quantitatively the V_g curves differ considerably.

Fig 6 $T\lambda$ -plots for unreacted ANFO on ZND theory.

Fig 7 $T\lambda$ -plots for detonation products of ANFO on ZND theory.

Figs 6 and 7 show the corresponding temperatures T_x and T_g respectively for the two thermal assumptions; the thermal equilibrium curves are, of course, identical in both figures, and exhibit an almost linear increase of temperature with λ .

6. DISCUSSION

The WBG is a complete EOS. It allows the temperature and the change of entropy to be calculated. The results show that while there is always a large increase of specific entropy on going from the explosive to products, in the case of thermal isolation the subsequent production of entropy in the reacted phase is very small because there is no heat conduction between the two phases. On the other extreme assumption there is an increase of entropy due to heat transfer from the hot products to the unreacted explosive. Heat conduction is essential for initiation, as pointed by Nutt [12], and the actual situation must lie between the two extremes.

The JWL can only be employed assuming thermal isolation, as the temperature is not defined. In this case its predictions do not differ dramatically from the more accurate WBG EOS. However, it cannot be used in more sophisticated calculations, for example, one in which the entropy production is minimized to find the balance between the two extreme assumptions, or another in which the heat transfer equation is coupled to the one-dimensional conservation equations and solved simultaneously.

ACKNOWLEDGEMENT

One of us (ZF) is grateful for the financial support of ICI Explosives Group Technical Centre, Ardeer, and to the British Council for a Scholarship (SBFSS scheme).

REFERENCES

- [1] Byers Brown, W. and Braithwaite, M., "Analytical Representation of the Adiabatic Equation for Detonation Products based on Statistical Mechanics and Intermolecular Forces", *Shock Compression of Condensed Matter 1991*, Elsevier, 325-328 (1992).
- [2] Byers Brown, W., "Analytical representation of the adiabatic equation for detonation products based on statistical mechanics and intermolecular forces" *Phil.Trans.Roy.Soc.A* **339**, 345-353 (1992).
- [3] Byers Brown, W., and Braithwaite, M., "Williamsburg Equation of State for Detonation Product Fluid", *Shock Compression of Condensed Matter 1993*, Colorado Springs, June 1993, S.C. Schmidt et al. Eds. (American Institute of Physics Press, 1994) pp.73-76.
- [4] Byers Brown, W., and Braithwaite, M., "Development of the Williamsburg Equation of State to model Non-ideal Detonation" *Proc. 10th Symposium (International) on Detonation*, Boston, Massachusetts, July 1993 (to be published)
- [5] Byers Brown, W., "Williamsburg Equation of State for Fluids at Very High Density", Contract Report for ICI plc Explosives Group Technical Centre, Ardeer (February 1994)
- [6] Freeman, T. L., Gladwell, I., Braithwaite, M., Byers Brown, W., Lynch, P.M., and Parker, I.B., "Modular Software for Modelling the Ideal Detonation of Explosives", *Math. Eng. Industry*, **3**, 97-109 (1991).
- [7] Parsafar, G., and Mason, E. A., "Universal Equation of State for Compressed Solids" *Phys Rev B* **49** 3049-3060 (1994)
- [8] Vinet, P., Ferrante, J., and Rose, J.H., "A Universal Equation of State for Solids", *J.Phys. C:Solid State Phys.* **19** L476-L473 (1986)
- [9] Vinet, P., Ferrante, J., Rose, J.H., and Smith, J.R., *J.Geophys.Res.* **92** 9319 (1987)
- [10] Vinet, P., Smith, J.R., Ferrante, J., and Rose, J.H., *Phys.Rev. B* **35** 1945-1953 (1987)
- [11] Fickett, W., and Davis, W.C., "Detonation" (University of California Press, 1979)
- [12] Nutt, G. L., "A Reactive Flow Model For A Monomolecular High Explosive", *J Appl Phys* **64** 1816-1826 (1988)