Analysis and prediction of initial state dependence for C−J state using unified EOS

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Abstract

It is well known that the detonation velocity for condensed-phase high energetic materials depends on the initial state, i.e., temperature and density. At present time, for the numerical simulations of the detonation physics, the parameter set of the equation of state (EOS) for the detonation products has to be prepared for each initial condition. However, if the complete reaction is assumed, the state surface has to be unique. We therefore have proposed the unified form EOS for detonation products. In this paper, the relationship between the initial temperature dependence of the detonation velocity and the initial density is examined using a proposed unified form of the EOS. The derivatives of the variables at Chapman -Jouguet (C−J) points are calculated by the unified form of the EOS. These derivatives are used to investigate the initial state dependence of the detonation velocity using the relationship between the detonation velocity and the initial state variables. As a result, the contributions of the coefficient of thermal expansion and the increment of the initial internal energy to the detonation velocity are clarified. We found that the initial temperature derivative of the detonation velocity can be estimated from the initial density derivative of the detonation velocity. In addition, the C−J pressures are estimated using the initial temperature dependence of the detonation velocity.

Keywords : initial state dependency of detonation, C−J hypothesis, J−M−S relation, PETN

1. Introduction

In the hydrodynamic computations of detonation physics of high-energetic materials, the parameter set of equation of state (EOS) for detonation products has to be prepared for each initial condition. However, if the complete reaction is assumed, the state surface has to be unique. It means that the EOS for detonation products essentially can be used without changing of parameters even if the initial state has changed. We therefore have started the investigation for the formulation of the EOS which can be applied for arbitrary initial conditions without changing any parameters. In previous study, we have proposed the unified form EOS which can be applied arbitrary initial densities using unique parameter set[1]. The proposed EOS was used for the reactive flow simulation for PETN[2].

In this paper, the basic theory for initial state dependence of the detonation velocity and our proposed unified method were described. The envelope approximation for initial temperature derivative of the detonation velocity was also described. Using proposed unified EOS, the initial temperature dependence of the detonation velocity was examined. In addition, the Chapman-Jouguet (C−J) pressures were estimated using the initial temperature dependence of the detonation velocity.

2. Theory
2.1 Initial state dependence of detonation velocity for high energetic materials[3,4]

The increment of the detonation velocity, D can be expressed as a function of the initial state variables v_0, ε_0, *and* P_0 as

$$\frac{dD}{D} = -A\frac{dv_0}{v_0} + B\frac{d\varepsilon_0}{D^2} - C\frac{dP_0}{\rho_0 D^2}$$
$$= \frac{\gamma-1-\alpha}{\alpha+2}\frac{dv_0}{v_0} + \frac{\alpha(\gamma+1)^2}{\alpha+2}\frac{d\varepsilon_0}{D^2} + \frac{\gamma+1}{\alpha+2}\frac{dP_0}{\rho_0 D^2} \quad (1)$$

where the variables v, ε, *and* P are the specific volume, specific internal energy, and pressure, respectively. The variables γ and α are defined at the C−J point, and are written as follows.

$$\gamma = -\frac{v}{P}\left(\frac{\partial P}{\partial v}\right)_S \quad (2)$$

$$\alpha = P\left(\frac{\partial v}{\partial \varepsilon}\right)_P \quad (3)$$

The subscript S denotes the isentrope line passing through the C−J point.

2.2 The unified method[1]

The derivative of Equation (1) with respect to the initial density can be written as follows.

$$\left(\frac{dD}{d\rho_0}\right)_{P_0} = -AD\frac{1}{v_0}\left(\frac{dv_0}{d\rho_0}\right) = ADv_0 \quad (4)$$

Here, the Jones assumption, $(\partial\varepsilon_0/\partial v_0)_{P_0} = 0$, is used. For a powdered explosive, many researchers have supported this assumption [3,4]. The variable A, the coefficient in first term of Equation (1) is the well-known Jones parameter and satisfies the relationship,

$$A = \frac{\rho_0}{D}\left(\frac{dD}{d\rho_0}\right)_{P_0} = \frac{\rho_0}{D}k \quad (5)$$

where following relationship between the detonation velocity and initial density was used [5].

$$D[\rho_0] = j + k\rho_0 \quad (6)$$

Here, j and k are constants.

We have proposed ordinary differential equations for the detonation products whose solution is the Grüneisen parameter as a function of the specific volume, in which following assumptions were employed. 1) The C−J hypothesis is valid. 2) The relationship between the detonation velocity and initial density is known, for example Equation (6). 3) The C−J state and isentropic line for detonation products for the theoretical maximum density (TMD) is known. By differentiating Grüneisen form EOS with respect to the specific volume, the following ordinary differential equation was obtained,

$$\frac{d\Gamma}{dv} = \frac{\Gamma(\Gamma+1)}{v} - \Gamma\frac{dP_S^{TMD}/dv + \rho_0^2 D^2}{P_{CJ} - P_S^{TMD}} \quad (7)$$

The value of P_{CJ} is obtained from the Rayleigh line ; thus, the above equation can be integrated along the C−J states from the C−J state at the TMD. Because the Equation (7) includes both the initial and C−J states, the ratio dv_0/dv is necessary to close the differential equations. The following relation, the JSM relation [6], was adopted to close the differential equation.

$$\Gamma = \frac{\gamma(\gamma-1-2A)}{(\gamma-A)} \quad (8)$$

The following differential equation can be obtained by differentiating Equation (8) with respect to the specific volume.

$$\frac{d\Gamma}{dv} = \frac{\rho_0(\gamma+1)}{(\gamma-A)^2} \times$$
$$\left[(\gamma+1)(2A^2-2A\gamma+\gamma^2+A) - \gamma\frac{dv_0}{dv}(3A^2-2A\gamma+\gamma^2)\right]. \quad (9)$$

The isentropic line passing through the C−J point for the TMD and the relationship between the detonation velocity and initial density were used to solve Equations (7) and (9). Since γ and α at the C−J state can be obtained simultaneously, it becomes possible to estimate the dependence of the detonation velocity on initial state for an arbitrary initial density. This approach will be applied for PETN. The JWL parameters for an initial density of $1.77\,\text{g/cm}^3$ are available [7]. Because this density is very close to the TMD for PETN, we regard this density as the TMD. We will adopt the following simple linear relationship between the initial density and detonation velocity in the analysis[5].

$$D = 0.1848 + 0.365\rho_0 \quad (10)$$

We call the method in this section the unified method in this paper.

2.3 Analysis of initial temperature dependence of detonation velocity

When an explosive is heated at a constant pressure, the second term of Equation (1) cannot be ignored. The derivative of Equation (1) with respect to the initial temperature can be written as

$$\left(\frac{dD}{dT_0}\right)_{P_0} = -AD\frac{1}{v_0}\left(\frac{dv_0}{dT_0}\right) + \frac{B}{D}\left(\frac{d\varepsilon_0}{dT_0}\right)_{P_0}$$
$$= -AD\beta_0 + \frac{B}{D}(C_{P_0} - P_{v_0}\beta_0) \cong -AD\beta_0 + \frac{B}{D}C_{P_0}, \quad (11)$$

where β_0 and C_{P_0} are the thermal expansion coefficient and the specific heat at constant pressure, respectively. The first term is the contribution of the thermal expansion, and the second term is the contribution of the increment of the initial specific internal energy. The term of $P_0 v_0 \beta_0$ was ignored because it is very small compared with the other contributions.

2.4 Envelope approximation[8]

The Rayleigh line from the initial state (v_0, ε_0) to C−J state is

$$P[v_0, \varepsilon_0] = \rho_0^2 D^2(v_0 - v) = Z^2[v_0, \varepsilon_0](v_0 - v), \quad (12)$$

where Z is the shock impedance. The variables in square brackets are independent variables. A variable at the left hand side of the square brackets is the function of these independent variables. The Rayleigh line from the point $(v_0 + \Delta v_0, \varepsilon_0)$ is

$$P[v_0 + \Delta v_0, \varepsilon_0] = Z^2[v_0 + \Delta v_0, \varepsilon_0](v_0 + \Delta v_0 - v). \qquad (13)$$

The envelope approximation can be obtained as the intersection of two Rayleigh lines of Equations (12) and (13) on P−v plane. Equating Equations (12) and (13), following equation is obtained.

$$\frac{D^2}{v_0^3}(2v - v_0)\,dv_0 + \frac{v_0 - v}{v_0^2}\,dD^2 = 0. \qquad (14)$$

From this equation, the relation between the initial temperature derivative of the detonation velocity can be derived, and can be written as follows under the condition of the constant initial pressure.

$$\left(\frac{\partial D}{\partial T_0}\right)_{P_0} = -\frac{D}{2v_0}\frac{2v - v_0}{v_0 - v}\left(\frac{\partial v_0}{\partial T_0}\right)_{P_0} = -\frac{D\beta_0}{2}(\gamma - 1) \qquad (15)$$

The envelope approximation has a simple form and can be estimated from the derivative γ.

3. Results and discussion

The relationship between the initial temperature derivative of the detonation velocity and the initial density for PETN is shown in Figure 1. The first and second terms of Equation (11) are plotted to clarify the contributions of the thermal expansion and increment of the initial internal energy. The result obtained by the envelope approximation is also plotted. The heating causes the thermal expansion, as a result the density decreases, so the detonation velocity decreases. Therefore, the first term takes a negative value. With decreasing initial density, the contribution of the first term decreases linearly. This is because the first term of Equation (11) can be written as the following expressions.

$$-AD\beta_0 = -\left(\frac{d\ln D}{d\ln \rho_0}\right)_{P_0}D\beta_0 = -k\rho_0\beta_0 \qquad (16)$$
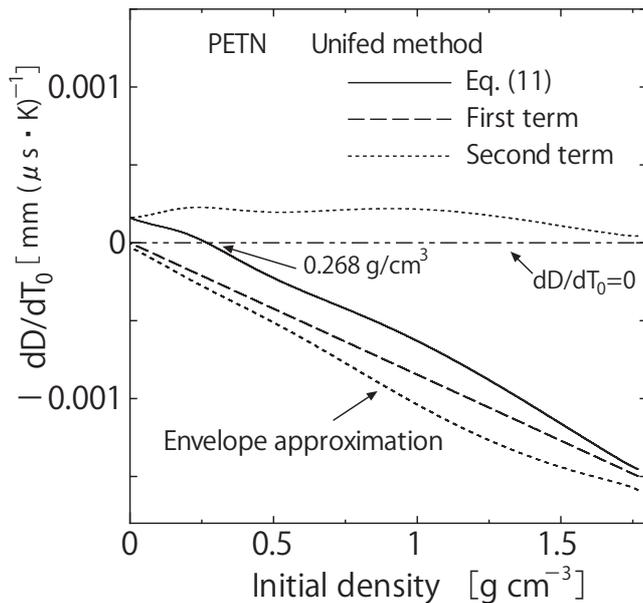
The first term is a more accurate approximation

Figure 1 Relationship between initial temperature derivative of detonation velocity and initial density for PETN obtained by unified method.
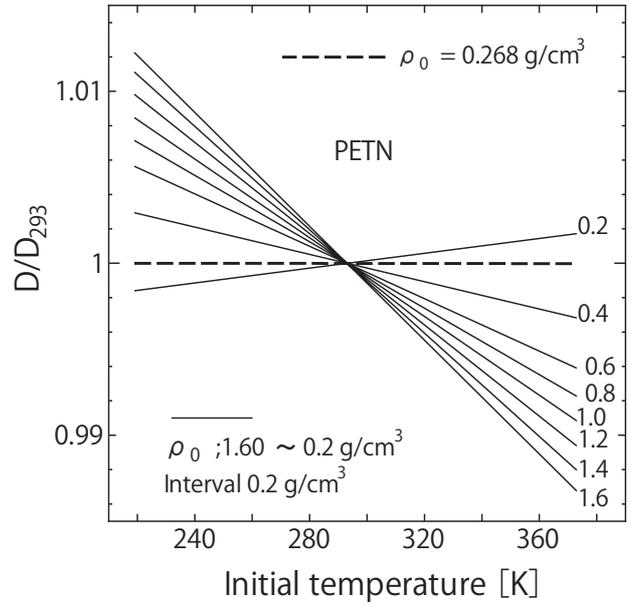

Figure 2 Detonation velocity vs. initial temperature for various values of initial density for PETN. D_{293}; detonation velocity at 293 K

compared with the envelope approximation. At a high initial density, the contribution of the thermal expansion is large. In contrast, the contribution of the increment of the internal energy is very small. The difference between the approximation by the first-term and Equation (11) is only about 3% near the TMD. That is, the formulation can be written as follows for the first-term approximation in the case of a high initial density.

$$\left(\frac{dD}{dT_0}\right)_{P_0} \cong -\left(\frac{dD}{d\rho_0}\right)_{P_0}\rho_0\beta_0 \qquad (17)$$

Since the contribution of the thermal expansion becomes small with decreasing initial density, the contribution of the internal energy becomes relatively large. The sign of the temperature derivative changes at an initial density of $0.268\,\text{g/cm}^3$.

The detonation velocity obtained by Equation (10) was regarded as the value at 293 K, and the initial temperature dependence of the detonation velocity is plotted in Figure 2, in which detonation velocity is divided by its value at 293 K. The relative contribution of the increment of the initial internal energy can be estimated from the ratio of the absolute values of the first and second terms as shown in Figure 3. When the ratio is one, the initial temperature derivative disappears. From Figures 2 and 3, it is clear that when the initial density is smaller than $0.6\,\text{g/cm}^3$, the contribution of the second term of the initial temperature derivative increases markedly. The ratio of the two terms can be written as

$$term\,2/|term\,1| = \frac{C_{P_0}}{k\beta_0}B\frac{1}{\rho_0 D}, \qquad (18)$$

where, according to our assumption, $C_{P_0}/k\beta_0$ is constant. The variation of the B with the initial density is small compared with that of $1/\rho_0 D$. That is, the inverse of the shock impedance is related to the contribution of the second term. Using Equation (6), the shock impedance can
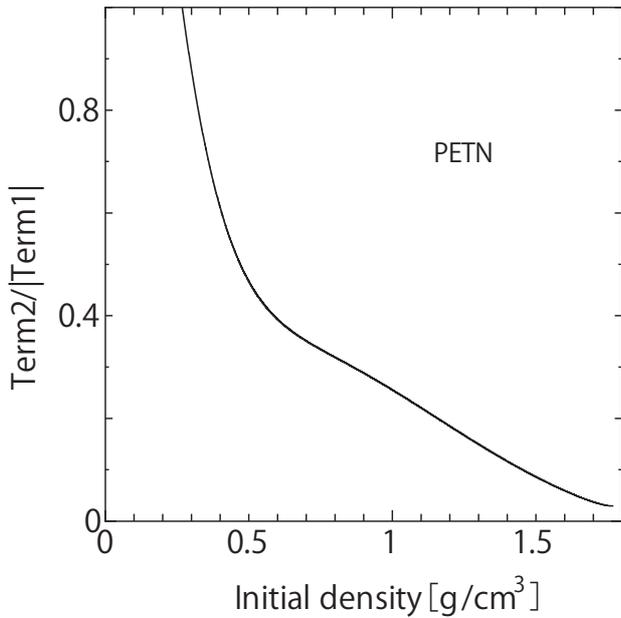
Figure 3   Relative contribution of increment of initial internal energy for PETN.
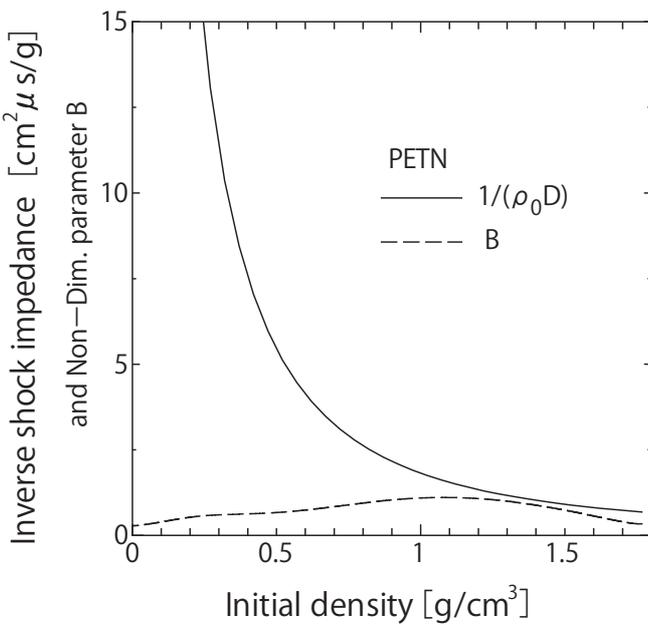(The ratio of first term to | second term | of Equation (11) vs. initial density)

Figure 4   Relationship between inverse of shock impedance and initial density for PETN.

be written as a quadratic equation in the initial density. The variation of the inverse of the shock impedance for PETN is shown in Figure 4 together with the variation of parameter B.

It can be seen that at low densities the inverse of the shock impedance markedly increases. At a low initial density, the large relative difference between the contributions of the thermal expansion and the increment of the internal energy is caused by the extremely small shock impedance of the detonation wave.

From the analysis of the initial temperature derivative of the detonation velocity for PETN, we found a very useful relationship between the initial temperature derivative and the initial density derivative, given as Equation (17). Near the TMD, the slope of the initial temperature derivative of the detonation velocity can be estimated from the first term of Equation (11). This implies that if a relationship between the initial density and detonation velocity exists, the initial temperature derivative of the detonation velocity can be estimated using the initial density dependence. The reverse is also true. Data for both the initial temperature and initial density derivatives for PBX9404 and LX04 are given in the LLNL Explosives handbook [5]. Using the experimental data for the initial density derivative, the values of the initial temperature derivative for these explosives are examined using Equation (11) and are compared with the experimental data in Table.1.

The differences between the experimental and predicted results are 1% or smaller. It can be concluded that for high-density powdered explosives, the first-term approximation can be accurately applied. For the above-mentioned two explosives, we attempted to estimate the derivative at the C−J point without the information obtained from the EOS. The unknown variables were γ and α. For this purpose, Equations (11) and (16) can be used to solve these variables. However, the values of α were negative and very close to zero. Under this condition, the thermal expansion coefficient has to be negative, meaning that physical meaning cannot be assigned to the result. Two situations can be considered. One is that the C−J hypothesis was failed, and the other is that the result was caused by experimental error. The measurement of detonation velocity is the most reliable means of obtaining the variables at the C−J state. To estimate the temperature derivative, however, high accuracy in the preparation of the sample is required. Therefore, in the investigation of detonation physics, experiments on the initial temperature derivative of the detonation velocity

Table 1   Measured initial temperature derivative and initial density derivative of detonation velocity, and initial temperature derivative of detonation velocity predicted by first-term approximation.

Explosive	$\Delta D / \Delta T_0$[5] $[cm \cdot (\mu s \cdot K)^{-1}]$	Density[5] $[g \cdot cm^{-3}]$	$\Delta D / \Delta \rho_0$[5] $[cm \cdot cm^3 \cdot (\mu s \cdot g)^{-1}]$	Cubic expansion[5] $[\mu cm \cdot (cm \cdot K)^{-1}]$	First term approximation (Eq.(16)) $\Delta D / \Delta T_0 [cm \cdot (\mu s \cdot K)^{-1}]$
PBX9404	-1.165×10^{-4}	1.84	0.36	174	-1.153×10^{-4}
LX−04	-1.550×10^{-4}	1.86	0.362	228.2	-1.545×10^{-4}

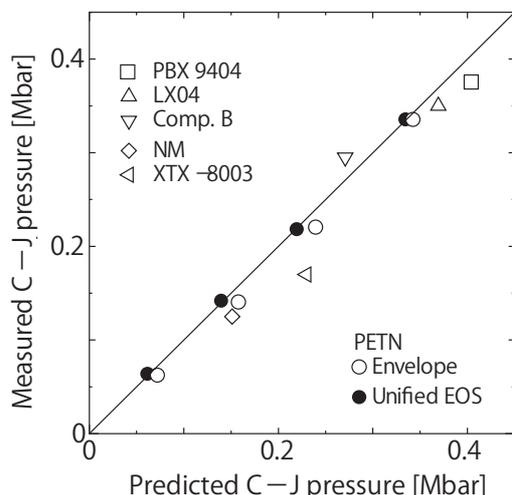**Figure 5**   Measured and predicted C－J pressures for various high explosives.

are still important for estimating reasonable values of α.

The C－J pressures for explosives whose initial temperature dependence of the detonation velocity is known were predicted by the envelope approximation. The formulation is as follows.

$$P = \rho_0 D^2 / (2(A+1)) \tag{19}$$

Here, we used the first-term approximation to obtain the value of A. That is, to predict the C－J pressure, the temperature derivative of the detonation velocity is also available. Five explosives for which the initial temperature dependence has been experimentally obtained were selected, and the estimated C－J pressures for these explosives are plotted in Figure 5.

In this figure, the results for PETN predicted from the envelope approximation using the initial density derivative and from the unified method are also plotted. Comparing with Equations (11) and (15), the envelope approximation requires the assumption of $\alpha = 0$. Therefore, the predicted pressure has to be slightly higher than the measured pressure. Although this was true for most of the measurements, there was the discrepancy for some data.

4. Conclusion

The relationship between the initial temperature dependence of detonation velocity and the initial density was examined by proposed unified form EOS. When this high energetic material was heated before the detonation under a constant pressure, the detonation velocity was governed by the contribution of the thermal expansion and the increment of the initial internal energy. The initial

temperature derivative of the detonation velocity is the sum of these two contributions, which have opposite signs. Near the TMD, the main effect of the contribution of the thermal expansion is to decrease the detonation velocity. In contrast, the contribution of the internal energy is very small. Under this situation, there is a relationship between the initial temperature derivative and the initial density derivative. Therefore, if a relationship between the initial density and the detonation velocity exists, the temperature derivative of the detonation velocity can be estimated using the initial density dependence. The reverse is also true. We called this the first-term approximation. With decreasing initial density, the contribution of the thermal expansion decreases linearly, which was expressed as a formula including the Jones parameter. Since the contribution of the thermal expansion becomes small together with decreasing initial density, the contribution of the internal energy becomes relatively large. At a low initial density, the relative difference between the contributions of the thermal expansion and the increment of the internal energy is caused by the extremely small shock impedance of the detonation wave. Finally, at a very low initial density, the sign of the initial temperature derivative changes from negative to positive. The first-term approximation was examined for PBX9404 and LX04 explosives, and we confirmed that it can be applied for these explosives. In addition, it was confirmed that the C－J pressures can be estimated by the envelope approximation using the initial temperature dependence of the detonation velocity.

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