



Shock and detonation properties of solid explosives with gaseous products

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ABSTRACT

We present a simple theoretical model to calculate shock and detonation properties of solid explosives. A solid equation of state of the Mie–Grüneisen form based on interatomic potential of the Lennard–Jones type with a soft repulsive part is used to calculate the shock properties of solid explosives. In conjunction with the Chapman–Jouguet condition, a reliable dense fluid equation of state and a simple mixing rule are used to calculate detonation properties of solid explosives with gaseous products. Calculations show a satisfactory agreement with experimental data and with results obtained from other theoretical modes.

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1. Introduction

When a solid explosive is shocked, its temperature, pressure and density rise sharply, consequently chemical reaction is triggered and a detonation wave is produced.

The Grüneisen equation of state is often used to describe the behavior of solids under compression,

$$P - P_c = \Gamma(E - E_c)\rho \quad (1)$$

P is the pressure, E is the specific internal energy (energy per unit mass) and ρ is the density. The subscript c refers to the cold contribution and Γ is the Grüneisen parameter (ratio), it is assumed to be a function of the specific volume. Several useful approximations for Γ based upon thermodynamic consideration and lattice dynamics are available [1–5], but the choice of a specific form among them is troublesome [6]. In spite of this troublesomeness, we have found that, in conjunction with an interatomic potential of the Lennard–Jones (LJ) type with a soft repulsive part, a general analytic expression of the Grüneisen parameter based on the Dugdale–MacDonald model is appropriate to describe properties of simple solids over a broad range of compression [7].

This Mie–Grüneisen equation of state is used to calculate shock properties of solid explosives. On the other hand, molecules in the product mixture of detonation products are assumed to interact via an “effective” LJ potential whose parameters are determined by a simple mixing rule, and hence a reliable dense fluid equation of

state, Hansen–Ree equation of state (HR–EoS) [8] is used to calculate detonation properties at the Chapman–Jouguet (CJ) state.

2. Theoretical

With the assumption that the shock wave is steady in time, the conservation of mass and momentum is expressed as,

$$\rho_0 u_s = \rho(u_s - u_p) \quad (2)$$

$$P - P_0 = \rho_0 u_s u_p \quad (3)$$

P , ρ , u_s and u_p are respectively, pressure, density, shock velocity and particle velocity. The subscript 0 refers to the initial state. Along with the conservation of energy, the above equations are used to obtain the Hugoniot relation,

$$E - E_0 = \frac{1}{2}(P + P_0)(V_0 - V) \quad (4)$$

where V is the specific volume ($V = 1/\rho$).

The unreacted (shock) Hugoniot is computed by finding a set of the thermodynamic variables (P , V , E) that satisfies the Hugoniot relation. Using the above equations, the Hugoniot relation can be presented either as a P – V relation or in the u_s – u_p plane.

Given the initial temperature (usually 298 K), and density, an equation of state of the Mie–Grüneisen type is used to calculate the initial internal energy. The specific internal energy and pressure of a solid can be written as,

$$E = E_c + E_{th} \quad (5)$$

$$P = P_c + P_{th} \quad (6)$$

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E_c and P_c are respectively, energy and pressure at zero temperature (0K). The subscript “th” refers to the contribution of thermal lattice vibration.

The calculation of the cold energy E_c begins with a priori assumption of the form of the interatomic potential. By summing the pair potential $\phi(r)$ over all atoms in the lattice [9,10],

$$E_c = \frac{1}{2} \sum n_i \phi(r_i) \quad (7)$$

n_i and r_i are the number of atoms and the corresponding radius of the i th shell of neighbors. For the Lennard-Jones potential of the general form [11],

$$\phi(r) = k(s)\varepsilon \left[\left(\frac{\sigma}{r} \right)^s - \left(\frac{\sigma}{r} \right)^6 \right] \quad (8)$$

with

$$k(s) = \left(\frac{6}{s-6} \right) \left[\frac{s}{6} \right]^{(s/(s-6))}$$

and for a face-centered cubic (fcc) lattice [10],

$$E_c(\rho^*) = \frac{1}{2} k(s) \left[C_s \left(\frac{\rho^*}{\sqrt{2}} \right)^{s/3} - \frac{1}{2} C_6 \rho^{*2} \right] \quad (9)$$

ρ^* is the reduced density (σ^3/V). The constants C_s (for different values of the repulsive exponent s) and C_6 are given in Hirschfelder et al. [9]. The repulsive exponent s has integer values greater than 6. The depth of the potential is ε and σ is the pair separation distance such that $\phi(0) = 0$.

As $P_c = -dE_c/dV$, then,

$$P_c(\rho^*) = \frac{1}{2} k(s) \left\{ \left[\frac{(s/3)C_s}{(\sqrt{2})^{s/3}} \right] \rho^{*(s/3+1)} - C_6 \rho^{*3} \right\} \quad (10)$$

While the cold compression energy represents a major part of the internal energy of a solid, the thermal energy associated with the vibrational motion of the atoms cannot be neglected. The quantity that characterizes the ratio of thermal pressure to thermal energy of the lattice defines the Gruneisen parameter Γ , i.e., Eq. (1) can be rewritten as,

$$P_{th} = \frac{\Gamma E_{th}}{V}$$

The Gruneisen parameter is usually assumed to be a function of volume only. Through some straightforward calculus manipulations [7], Eq. (10) is used to obtain an expression for Γ_{DM} in terms of the potential parameters (Eq. (8)).

If the temperature is above several hundreds of degrees kelvin, quantum effects play no role in the vibrations and the vibrational energy is equal to its classical value of $3kT$. Then, one can write the well-known Mie–Gruneisen EoS as,

$$E = E_c + 3NkT \quad (11)$$

$$P = P_c + \frac{\Gamma}{V}(3NkT) \quad (12)$$

Detailed analysis [7] has shown that an interatomic potential of the form (8) with a soft repulsive part ($s=7$) is appropriate to describe solid properties over a broad range of compression.

Detonation properties are calculated by applying the Chapman–Jouguet (CJ) condition which chooses from all possible solution to the conservation equations the one that corresponds to the propagation with the lowest velocity, the detonation velocity. The application of CJ condition to determine the CJ state requires a complete knowledge of thermodynamic properties of detonation products. A reliable analytical representation of the thermodynamic properties of molecules interacting via LJ potential was

provided by Ree [8]. This constitutive relationship fits a large number of computer simulated data over a wide range of density and temperature. Hansen–Ree equation of state (HR-EOS) takes the form,

$$\frac{\beta P}{\rho^*} = \frac{\beta P_{rep}}{\rho^*} - \left(\frac{1}{T^*} \right)^{1/2} \sum_{i=1}^5 i C_i X^i + \left(\frac{1}{T^*} \right) \sum_{i=1}^5 D_i X^i \quad (13)$$

where

$$\frac{\beta P_{rep}}{\rho^*} = 1 + B_1 X + B_2 X^2 + B_3 X^3 + B_4 X^4 + B_{10} X^{10}$$

Here, $\beta = 1/kT$ and $X = \rho^*/T^{*(1/4)}$. ρ^* and T^* are respectively, the reduced density and temperature ($T^* = kT/\varepsilon$, k is Boltzmann constant). The constants B , C , and D are given elsewhere [8].

From the dense fluid equation of state, Eq. (13), and the following thermodynamic relation,

$$T \left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial E}{\partial V} \right)_T + P$$

an expression of the excess internal energy (after subtracting the dilute gas contribution) in terms of density and temperature can be obtained. The dilute gas contribution to the internal energy E_{dil} is given by [12],

$$E_{dil} = \frac{3}{2} RT + \frac{r}{2} RT + R \sum_{i=1}^{\alpha} \left(\frac{\theta_{vi}}{2} + \frac{\theta_{vi}}{\exp(\theta_{vi}/T) - 1} \right)$$

r is the number of rotational degrees of freedom (two for linear molecules and three for nonlinear molecules), θ_v is the characteristic vibrational temperature, $\theta_v = h\nu/k$, and α is the number of vibrational degrees of freedom. Values of θ_v for various product species are taken from [12].

Molecular mixture of detonation products at the CJ state is assumed to interact via the LJ potential with effective potential parameters provided by the simple mixing rule [13],

$$\begin{aligned} \sigma_{mix}^3 &= \sum_{ij} n_i n_j \sigma_{ij} \\ \varepsilon_{mix} \sigma_{mix}^3 &= \sum_{ij} n_i n_j \varepsilon_{ij} \sigma_{ij}^3 \end{aligned} \quad (14)$$

Here, n_i is the mole fraction. Force constants between unlike molecules are related to those between molecules of the same type through,

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad \text{and} \quad \varepsilon_{ij} = (\varepsilon_{ii} \varepsilon_{jj})^{1/2}$$

In order to compare the calculations with experimental data, quantities have to be converted into dimensional ones. This is done through the “effective” LJ potential parameters: for the detonation velocity, $D_{CJ} = D_{CJ}^* (\varepsilon_{mix}/M)^{1/2}$ and for the detonation pressure, $P_{CJ} = P_{CJ}^* (\varepsilon_{mix}/\sigma_{mix}^3)$ where M is the “effective” molecular weight, $M = \sum_{ij} n_i m_i$. Here m_i is the molecular weight of the i th component.

3. Results and discussion

The present theoretical model is tested by calculating shock and detonation properties of solid explosives and comparing the theoretical predictions with the available experimental data and with other theoretical calculations. HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) and AN (ammonium nitrate) are representative examples. HMX is reasonably complex high explosive containing important products common to many other explosives. Major detonation products: N_2 , CO_2 , H_2O , NH_3 , CH_4 and many other minor

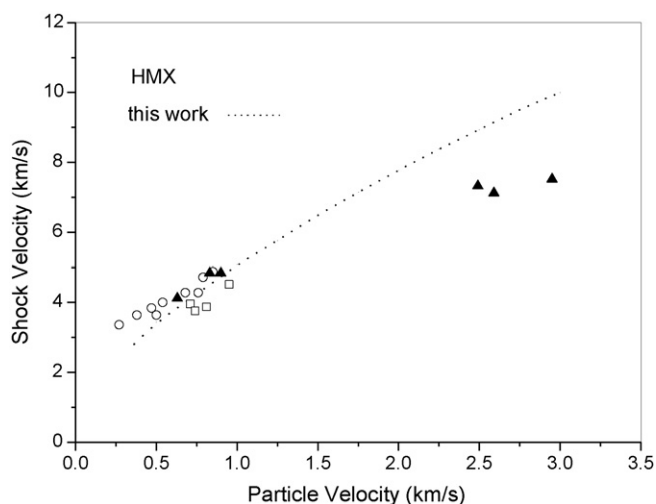


Fig. 1. Computed shock Hugoniot of HMX compared with experimental data and with other calculations. Circles: Olinger et al.; triangles: single crystal; squares: Simpson et al. (calculated data using JWL-EoS). Sources of experimental data and other calculations are as cited in Bernecker.

amount of chemical species which are mostly gas up to moderate loading densities. On the other hand, the detonation products of AN are very few, mostly H_2O , N_2 and O_2 [14].

Unreacted Hugoniot of high explosives is difficult to measure and experimental data are scarce. However, unreacted Hugoniot can be deduced from the Hugoniot data of mixtures containing HMX. Since the Hugoniot data for mixtures exist only for some porous state, these experimental data points for mixtures are first corrected to the voidless state [15]. Each datum must be viewed in this context.

The computed u_s-u_p shock Hugoniot of HMX is compared with experimental data and with other theoretical calculations in Fig. 1. Sources for each class of experimental data are as cited in Bernecker [15] and conditions for each are described therein. The initial density used in the present calculation is 1.9 g/cm^3 and the LJ parameters of the HMX molecule yield the best agreement with experimental results as $\sigma = 0.7500 \text{ nm}$ and $\epsilon/k = 1280 \text{ K}$. These values are reasonable, compared to those obtained from the measured viscosity and second virial coefficient for much simpler molecules [9]. However, for such a large molecule, these parameters are merely considered as adjustable ones.

As Fig. 1 indicates, the agreement between theoretical predictions and experimental data, except in the upper range of u_s-u_p Hugoniot, is good. The Hugoniot data deduced by Olinger et al. are from their isothermal compressibility data [15]. Bernecker calculated Hugoniot data for voidless HMX from experimental data of pressed samples of both neat HMX and its various mixtures. Bernecker's work [15] indicates that HMX Hugoniot has two linear regions in the u_s-u_p plane.

Detonation properties are calculated by applying the Chapman–Jouguet condition which is equivalent to the statement that the straight line (Rayleigh line) from the initial state at V_0 is tangent to the reacted (detonation) Hugoniot. The initial specific energy E_0 is computed using the Mie–Grüneisen EoS (Eq. (11)) and the dense fluid EoS (Eq. (13)) is used to calculate the thermodynamic properties of detonation product mixture whose effective potential parameters are obtained through the mixing rule (Eq. (14)). Detonation properties of HMX is computed assuming the same detonation products at various loading densities (Table 1). This implies a constant heat of reaction, 1453.3 cal/g [14].

Table 1

Major detonation product species of HMX and AN along with the corresponding potential parameters [9,14].

Product species	Mole fraction	σ (nm)	ϵ/k (K)
HMX			
N_2	0.381	0.3698	79.8
CO_2	0.308	0.3897	205.0
H_2O	0.172	0.3000	135.0
NH_3	0.044	0.3000	135.0
CH_4	0.031	0.3817	137.0
AN			
H_2O	0.571	0.3000	135.0
N_2	0.286	0.3698	79.8
O_2	0.143	0.343	88.0

Using values of product mole fractions given in Table 1, the computed “effective” potential parameters of the product mixture are $\sigma_{\text{mix}} = 0.3465 \text{ nm}$ and $\epsilon/k = 131.950 \text{ K}$. The Chapman–Jouguet velocity D_{CJ} , pressure P_{CJ} , and temperature T_{CJ} are calculated and compared with experimental results [16–19] in Figs. 2–4 respectively. As Fig. 2 indicates, the calculated D_{CJ} is in satisfactory agreement with the experiment up to loading density of about 1.2 g/cm^3 , above which solid carbon starts to appear as a major detonation product [14]. Present calculations are designed to handle solid explosives with gaseous products.

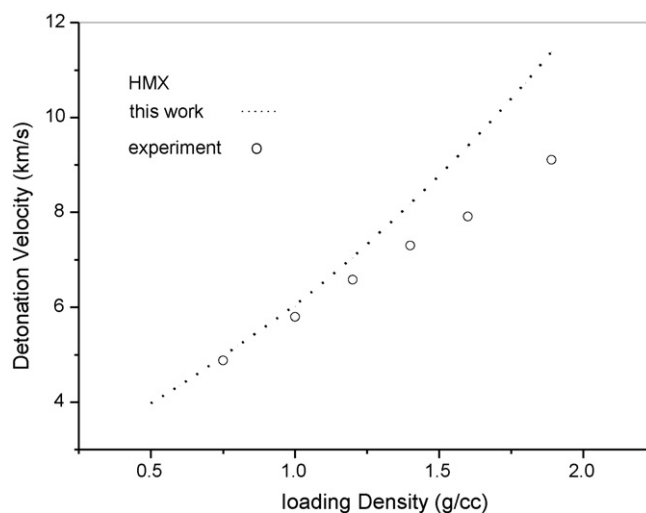


Fig. 2. Detonation velocity of HMX as a function of loading density.

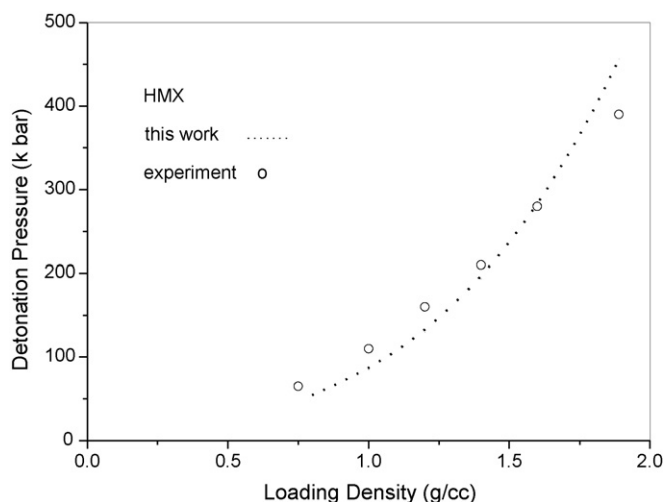


Fig. 3. Detonation pressure of HMX as a function of loading density.

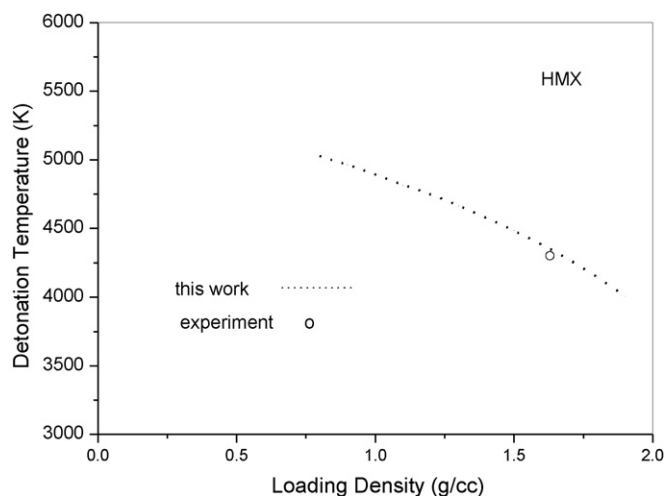


Fig. 4. Detonation temperature of HMX as a function of loading density.

The comparison between calculated and measured detonation pressure of HMX is depicted in Fig. 3. Sources for experimental data are as cited in Hobbs and Baer [18]. As the figure indicates, the overall agreement between theoretical predictions and experiment is satisfactory. However, the comparison between Figs. 2 and 3 indicates that detonation velocity is more sensitive to the existence of solid carbon as one of the detonation products.

While the experimental data on detonation velocity of HMX are so copious and that of detonation pressure are available over a wide range of loading density, the experimental data on detonation temperature are difficult to find. Theoretical calculation of detonation temperature reveals a monotone decrease in temperature with increasing initial (loading) density, a behavior observed for many high explosives [19]. The agreement between calculations and the available experimental temperature at $\rho = 1.63 \text{ g/cm}^3$ is excellent [17].

It should be emphasized that the same values for the potential parameters of HMX molecule: $\sigma = 0.7500 \text{ nm}$ and $\varepsilon/k = 1280 \text{ K}$, are used for both shock and detonation calculations which are two independent calculations, and the overall agreement between experiment and theoretical predictions is satisfactory in both cases. This places some confidence in the present theoretical model.

The present model is further tested by calculating detonation properties of ammonium nitrate AN. Unfortunately, the available experimental data in this case are scarce. Therefore, the present calculations are mainly compared with those of other theoretical models.

AN is one of the less sensitive of all explosives. Besides the economic features of this explosive, the reduction in relative hazard is connected with the increase of its content in explosives.

Contrary to the HMX explosive, AN has very few detonation product species. The fixed detonation products of AN listed in Table 1 along with the corresponding mole fractions, heat for reaction [14], and potential parameters [9] are used to compute detonation properties of AN. The potential parameters of the AN molecule are $\sigma = 0.4890 \text{ nm}$ and $\varepsilon/k = 300 \text{ K}$, while the "effective" parameters of the detonation products mixture are $\sigma_{\text{mix}} = 0.3276 \text{ nm}$ and $(\varepsilon/k)_{\text{mix}} = 107.13 \text{ K}$.

As the experimental data are so scarce, the present calculations are mainly compared with other theoretical calculations. As Figs. 5 and 6 indicate, detonation velocity and pressure are in good agreement with theoretical predictions from BKW-EoS, LJD-EoS [20] and with Tanak's calculations [14]. The only available experimental data point, detonation velocity at $\rho_0 = 1.05 \text{ g/cm}^3$, is in

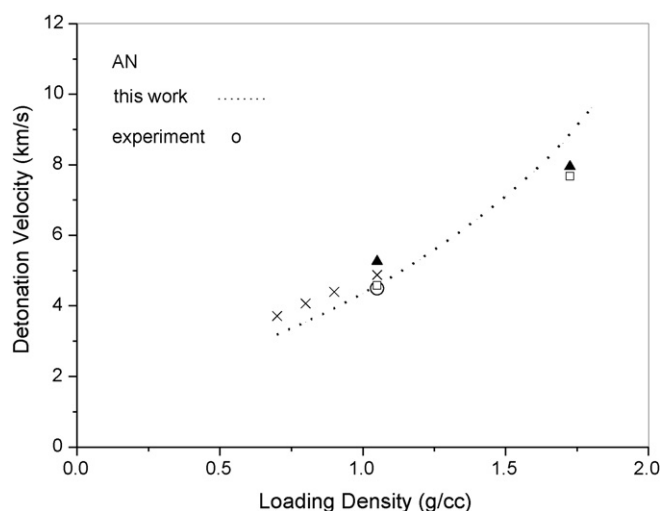


Fig. 5. Computed detonation velocity of AN as a function of loading density compared with experimental results (o) and with other calculations (crosses: Tanak's; triangles: BKW-EoS; squares: LJD-EoS).

excellent agreement with predictions from the present model, the experimental value is 4.50 km/s [20] while the calculated one is 4.58 km/s .

Detonation temperature of AN as calculated using the present model is compared with other theoretical predictions in Fig. 7. In spite of the scatter of the data points, all theoretical models predict a monotone decrease in temperature with increasing initial density.

It is worth emphasizing that the same values for the potential parameters of the shared detonation product species in both case, HMX and AN (Table 1), are used to calculate detonation properties of the two explosives and the overall agreement between experiment and theoretical predictions is satisfactory. This places more confidence in the present theoretical model.

Before closing this discussion we should mention that we previously [7] presented a preliminary test for this model as we used it to calculate detonation properties of PETN (pentaerythritol tetranitrate) high explosive. Because of the high oxygen content of PETN, its detonation products should be almost all gaseous and consequently it is an excellent example to examine the present model. In fact, the comparison of theoretical predictions with experimental

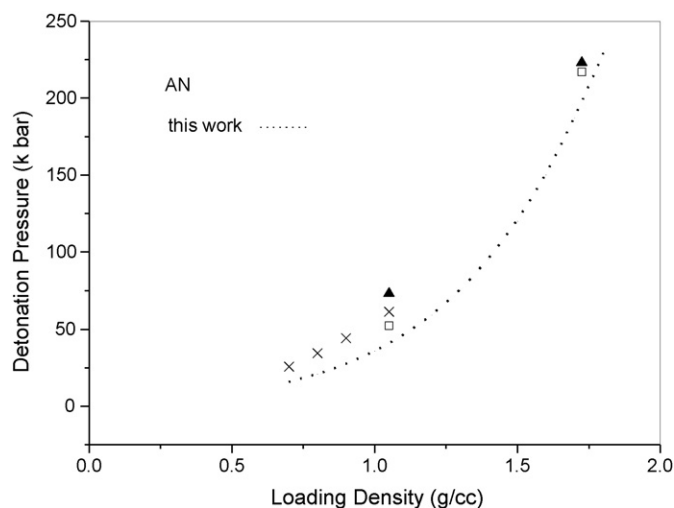


Fig. 6. Computed detonation pressure of AN as a function of loading density compared with other calculations (crosses: Tanak's; triangles: BKW-EoS; squares: LJD-EoS).

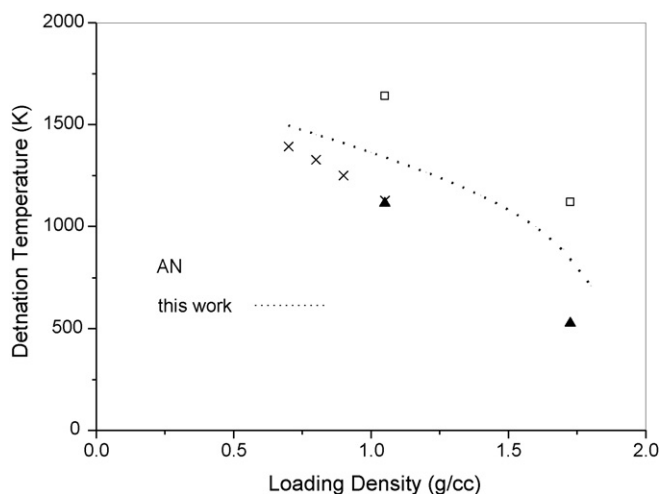


Fig. 7. Computed detonation temperature of AN as a function of loading density compared with other calculations (triangles: BKW-EoS; squares: LJD-EoS).

data over a wide range of initial density reveals that the present model provides an adequate description of detonation properties of PETN.

4. Conclusion

Shock and detonation properties of solid explosives with gaseous products could be adequately described by a simple theoretical model. The model is based upon a solid equation of state of the Mie–Grüneisen form with an interatomic potential of the Lennard–Jones type with a soft repulsive part and a reliable dense fluid equation of state. The solid equation of state is used to calculate the shock properties of the compressed solid and in conjunction with a simple mixing rule, the dense fluid equation of state is used to calculate detonation properties.

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