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A Micro-macro Coupling Approach of MD-SPH Method for Reactive Energetic Materials

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Abstract. The simulation of reactive energetic materials has long been the interest of researchers because of the extensive applications of explosives. Much research has been done on the subject at macro scale in the past and research at micro scale has been initiated recently. Equation of state (EoS) is the relation between physical quantities (pressure, temperature, energy and volume) describing thermodynamic states of materials under a given set of conditions. It plays a significant role in determining the characteristics of energetic materials, including Chapman-Jouguet point and detonation velocity. Furthermore, EoS is the key to connect microscopic and macroscopic phenomenon when simulating the macro effects of an explosion. For instance, an ignition and growth model for high explosives uses two JWL EoSs, one for solid explosive and the other for gaseous products, which are often obtained from experiments that can be quite expensive and hazardous. Therefore, it is ideal to calculate the EoS of energetic materials through computational means. In this paper, the EoSs for both solid and gaseous products of β−HMX are calculated using molecular dynamics simulation with ReaxFF-d3, a reactive force field obtained from quantum mechanics. The microscopic simulation results are then compared with experiments and the continuum ignition and growth model. Good agreement is observed. Then, the EoSs obtained through micro-scale simulation is applied in a smoothed particle hydrodynamics (SPH) code to simulate the macro effects of explosions. Simulation results are compared with experiments.

INTRODUCTION

The EoS plays a significant role in determining the characteristics of energetic materials, including Chapman-Jouguet point and detonation velocity [1]. It is the key to connect microscopic and macroscopic phenomenon in the study of energetic materials. In addition, EoS is the foundation of many numerical models for high explosives. For example, JWL++ model consists of two EoSs, one for solid explosive and the other for gaseou products [2]. The two EoSs are mixed using a simple additive rule. Similarly, the ignition and growth model also consists of two JWL EoSs, one for solid explosive and the other for gaseous products [3]. The difference is that in the ignition and growth model, two physical assumptions (temperature equilibrium and pressure equilibrium) are introduced, which make the mixture rule much more complex but also much more accurate than JWL++ model. Both of the two models are widely used for numerical modeling of high explosives.

Molecular dynamics is a powerful tool to investigate many microscopic processes. In recent years, the detonation of high explosives has been explored much more profoundly with the introduction of reactive force fields (ReaxFF) in molecular dynamics [4]. Furthermore, Liu et al introduced an additional vdW-like interaction to ReaxFF, which enables ReaxFF to obtain the correct density of molecular crystals [5]. In the paper, both the EoSs of solid and gaseous products of β−HMX are calculated using ReaxFF-d3, a reactive force field obtained by quantum mechanics. Then, the calculated EoSs are compared with experiment [6], and EoSs in ignition and

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growth model [7]. Good agreement is observed. Then, the calculated EoSs are applied in smoothed particle hydrodynamics (SPH) code to simulate the macro scale explosion of PBX 9501.

MOLECULAR DYNAMICS SIMULATION

Structure and relaxation of β−HMX

We focus on the β-HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), a typical secondary explosive whose chemical formula is $C_4H_8N_8O_8$. The β-HMX used for molecular dynamics simulation is obtained from our previous DFT-D2 study [8]. The lattice constants of unit β-HMX are listed in Table.1.

TABLE 1. Lattice constants of β-HMX from experiment [9] and DFT-D2 calculations [8]

	a (Å)	b (Å)	c (Å)	α	β	γ
Experiment [9]	6.54	11.05	8.70	90°	124.30°	90°
DFT-D2 [8]	6.542	10.842	8.745	90°	124.41°	90°

The supercell of β-HMX consists of 64 β-HMX molecules, which contains 1792 atoms in total. The density of β-HMX before relaxation is 1893.4 kg/m^3. Three ensembles (NPT, NVT, NVE) are used successively to relax the system. Each ensemble takes 50 ps. In the relaxation, the temperature is controlled at around 300K to prevent potential phase transformation. After relaxation, the volume of β-HMX is 16924.73 Å^3 (density is 1859.4 kg/m^3, which is very close to experiment value 1830 kg/m^3 [10]).

Hugoniot EoS of solid explosive

The Hugoniot EoS describes the locus of thermodynamics states of solid explosives with shock wave passing through. In the ignition and growth model [7], the EoS for solid explosive is derived from the Hugoniot curve, which can be expressed as:

$$p_s = A_s \cdot e^{-r_{1s}v} + B_s \cdot e^{-r_{2s}v} + \frac{\omega_s C_{Vs} T}{v} \qquad (1)$$

where *As, Bs,* r_{1s}, r_{2s}, and ω_s are parameters fitted based on experimental data, C_{Vs} is the specific heat of the solid explosive, T is temperature, ν is specific volume, and p_s is the pressure of solid explosive. It can be seen that temperature is introduced in the expression, which differs from traditional EoS of solid explosive [2].

The JWL EoS parameters for PBX 9501 are listed in Table 2 [7]. PBX 9501 is chosen because it consists of 95 weight % HMX, 2.5 weight % estane binder, and 2.5 weight % BDNPA/F.

TABLE 2. Parameters of JWL EoS of solid PBX 9501 [7].

	A_s (GPa)	B_s (GPa)	r_{1s}	r_{2s}	ω_s	C_{Vs} (J / (kg•K))	T_0 (K)
Solid PBX 9501	732000	-5.2654	14.1	1.41	0.8867	2.7806 x 10^6	298

To obtain the EoS of solid β−HMX, a series of NVT simulations is performed. According to Yoo [6], the pressure-volume relation obtained under hydrostatic conditions should be in good agreement with Hugoniot curve. The simulation scheme is as follows: compress the β-HMX along the a-direction of the supercell to a predefined volume at 300 K, thus, for each volume, there is a corresponding pressure. In the implementation of each NVT simulation, the time step is set to be 0.1 fs and the total simulation time is 15 ps. The comparison of JWL EoS of solid PBX 9501 [7] with experiment [6] and the calculated EoS of solid β−HMX by MD is shown in Fig. 1.

It can be seen from Fig.1 that at 300K, the EoS calculated by MD is quite close to Yoo's experiment at high volume ratio (greater than 0.97). However, it gradually deviates from experiment when volume ratio is less than 0.97. The EoS calculated by molecular dynamics is greater than EoS of solid PBX 9501 when volume ratio is greater than 0.725. When the volume ratio is smaller than 0.725, the case is opposite. It is probably because that PBX 9501 contains 95% HMX and 5% other materials (whose density is around 1050 kg/m^3, smaller than the density of HMX, which is 1910 kg/m^3).

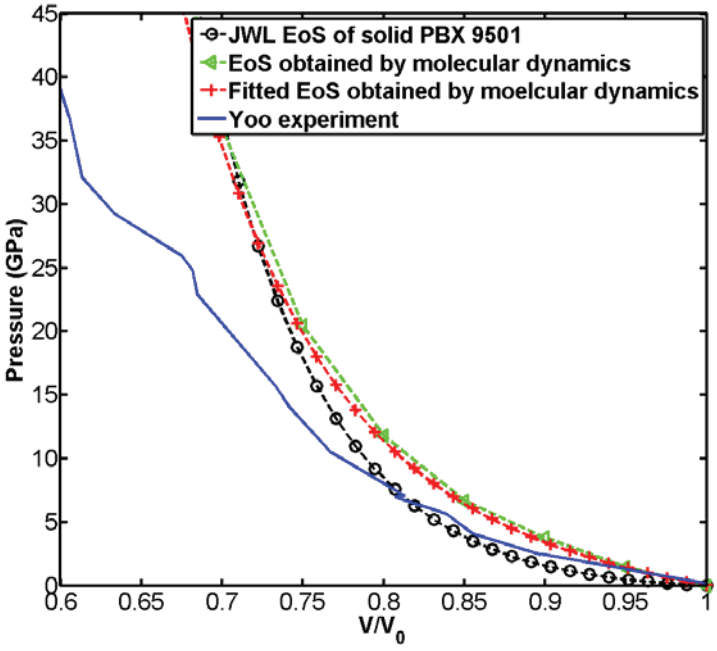

FIGURE 1. Comparison of the JWL EoS of solid solid PBX 9501 [7] with experiment [6] and EoS of solid β−HMX by MD. It should be noted that Yoo's experiment is conducted at room temperature.

JWL EoS of gaseous products of explosive

Similarly, a series of NVT simulation is conducted to obtain the JWL EoS of gaseous products of β−HMX. It should be noted that prior to NVT simulation, NPHUG [11] is used to compress the supercell of β−HMX to around 64 GPa. Afterwards, the system is dilated from compressed state using NVT ensemble. The simulation scheme is as follow: dilate the compressed β-HMX along a specific direction (a-direction of the supercell) to reach a predefined volume at 3000 K, thus, for each volume, there is a corresponding pressure. The time step is set to be 0.1 fs and the total simulation time is set to be 15 ps.

In the ignition and growth model [7], the JWL EoS of gaseous products of high explosives has a similar form as the JWL EoS of solid explosive:

$$p_g = A_g \cdot e^{-r_{1g}v} + B_g \cdot e^{-r_{2g}v} + \frac{\omega_g C_{Vg} T}{v}, \qquad (2)$$

where p_g is the pressure of the gaseous products. The other parameters have a similar meaning as those in Eq. (1). The parameters of JWL EoS of gaseous products of PBX 9501 are listed in Table 3 [7].

TABLE 3. Parameters of JWL EoS of gaseous products of PBX 9501 [7].

	A_g (GPa)	B_g (GPa)	r_{1g}	r_{2g}	ω_g	C_{Vg}(J /(kg•K))	T_0 (K)
Gaseous PBX 9501 products	1668.9	59.69	5.9	2.1	0.45	1.0 x 10^6	298

The comparison of JWL EoS of gaseous products of PBX 9501 [7] with EoS of β−HMX obtained from MD simulation is shown in Fig. 2. It should be noted that the predefined temperature is 3000 K, which is close to the temperature of gaseous products of PBX 9501 right after explosion.

It can be seen from Fig. 2 that the EoS calculated via MD agrees very well with JWL EoS of gaseous products of PBX 9501 in the ignition and growth model.

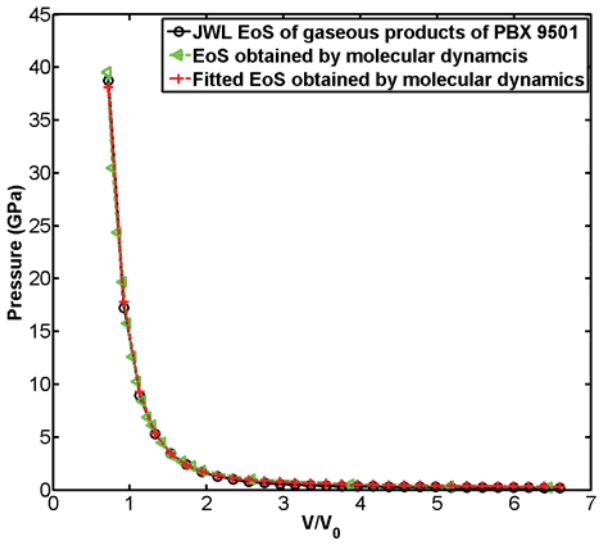

FIGURE 2. Comparison of the JWL EoS of gaseous products of PBX 9501 [7] with the EoS obtained from MD. The temperature is set to be 3000 K.

THE APPLICATION OF EOS IN SMOOTHED PARTICLE HYDRODYNAMICS

Smoothed particle hydrodynamics (SPH) is a mesh-free Lagrangian method excelling in the simulation of moving interfaces and large deformation [12], which is common in high-velocity impact and explosion. The governing equations for hydrodynamics problems are Navier-Stokes equations. The standard Navier-Stokes equations consist of the following equations [12]:

$$\begin{cases} \dfrac{\mathrm{d}\rho}{\mathrm{d}t} = -\rho_i \sum_{j=1}^{N} \dfrac{m_j}{\rho_j} \boldsymbol{v}_j^{\beta} \dfrac{\partial W_{ij}}{\partial \boldsymbol{x}_i^{\beta}}, & \text{Continuity Equation (3)} \\ \dfrac{\mathrm{d}\boldsymbol{v}_i^{\alpha}}{\mathrm{d}t} = -\sum_{j=1}^{N} m_j \left(\dfrac{\sigma_i^{\alpha\beta}}{\rho_i^2} + \dfrac{\sigma_j^{\alpha\beta}}{\rho_j^2} + \Pi_{ij} \right) \dfrac{\partial W_{ij}}{\partial \boldsymbol{x}_i^{\beta}}, & \text{Momentum Equation (4)} \\ \dfrac{\mathrm{d}e_i}{\mathrm{d}t} = \dfrac{1}{2} \sum_{j=1}^{N} m_j \left(\dfrac{p_i}{\rho_i^2} + \dfrac{p_j}{\rho_j^2} \right) (\boldsymbol{v}_i^{\beta} - \boldsymbol{v}_j^{\beta}) \dfrac{\partial W_{ij}}{\partial \boldsymbol{x}_i^{\beta}} + \dot{q}, & \text{Energy Equation (5)} \end{cases}$$

where ρ is the density, e is the specific internal energy, ν^{α} is velocity, and $\sigma^{\alpha\beta}$ is the total stress tensor, which are all dependent variables. $\varepsilon^{\alpha\beta}$ is the strain rate tensor, Π is artificial viscosity, $\boldsymbol{x}^{\alpha}$ is spatial coordinate and t is time. $\dot{q}$ is the heat release rate, which plays a critical role in transition of shock wave to detonation wave.

Two physical assumptions, pressure equilibrium and temperature equilibrium, are introduced in the ignition and growth model, which can be described as follows:

$$p = p_s = p_{\mathrm{g}} \tag{6}$$

$$T = T_s = T_{\mathrm{g}} \tag{7}$$

It means that in the detonation of high explosives, the pressure and temperature of solid explosive and gaseous products should always be equal, except in the initial stage and in final stage. In the initial stage, there only exists solid explosive while in the final stage, there only exists gaseous products.

The reaction rate can be described as follows:

$$\frac{\mathrm{d}\lambda}{\mathrm{d}t} = \lambda_1 + \lambda_2 + \lambda_3 \tag{8a}$$

$$\lambda_1 = I(1-\lambda)^b \left(\frac{\rho}{\rho_0} - 1 - a \right)^x, 0 < \lambda < \lambda_{ig\max} \tag{8b}$$

$$\lambda_2 = G_1(1-\lambda)^c \lambda^d p^y, 0 < \lambda < \lambda_{G1\max} \tag{8c}$$

$$\lambda_3 = G_2(1-\lambda)^e \lambda^g p^z, 0 < \lambda < \lambda_{G2\max} \tag{8d}$$

where I, a, b, x, c, d, y, e, g, z, G_1, G_2, $\lambda_{ig\,max}$, $\lambda_{G1\,max}$, and $\lambda_{G2\,max}$ are rate constants, ρ is the current density, ρ_0 is the density of solid explosive, and λ is the mass fraction of gaseous products. The reaction rate parameters [7] are given in Table 4, and the comparison of fitted JWL EoSs parameters with the original in ignition and growth parameters [7] is listed in Table 5.

TABLE 4. Reaction rate parameters for PBX 9501 [7].

Parameter	Value
I	1.4×10^{17} s^{-1}
a	0.0
b	0.667
x	20.0
c	0.667
d	0.277
y	2.0
e	0.333
g	1.0
z	2.0
G_1	130×10^{-16} Pa^{-y} s^{-1}
G_2	400×10^{-16} Pa^{-z} s^{-1}
$\lambda_{ig\,max}$	0.3
$\lambda_{G1\,max}$	0.5
$\lambda_{G2\,max}$	0.5

TABLE 5. Comparison of fitted JWL EoS parameters with original parameters in ignition and growth model.

	JWL EoS of solid explosive		JWL EoS of gaseous products	
	original	fitted	original	fitted
A	732000 GPa	129230 GPa	1668.9 GPa	1015 GPa
B	-5.2654 GPa	-0.3678 GPa	59.69 GPa	85.1 GPa
r_1	14.1	11.8767	5.9	5.3546
r_2	1.41	-2.4892	2.1	2.5254
ω	0.8867	4.2431	0.45	0.7041

The experiment is depicted as follows [7]: A 100 mm diameter, 12.5 mm thick aluminum flyer plate impacts a target consisting of: a 90 mm diameter, 6 mm thick aluminum plate, a 90 mm diameter, 20 mm thick PBX 9501 charge, and a 90 mm diameter, 6 mm thick aluminum back plate. Pressure gauges are embedded in the explosive bar to record the variation of pressure in detonation.

The 1D PBX 9501 model is 0.02 m long, as shown in Fig. 3. There is a rigid wall on the left. The explosive bar will impact the wall at a certain velocity. Particles are distributed evenly, smoothing length is set to be 1.5 times distance between two neighboring particles. The model consists of 4000 particles.

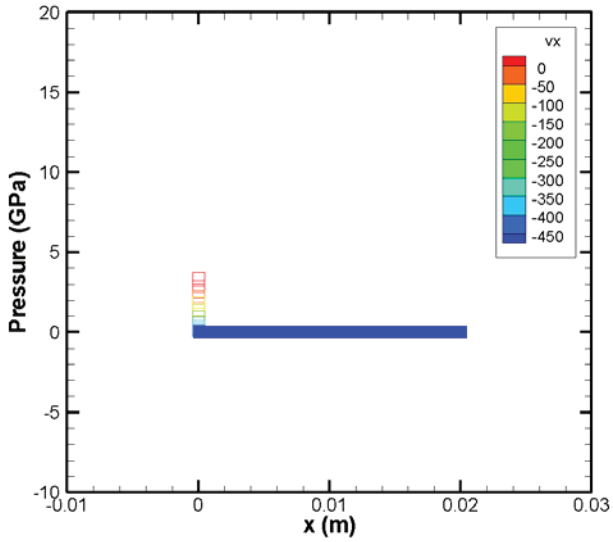

FIGURE 3. SPH model of the 1D PBX 9501 bar.

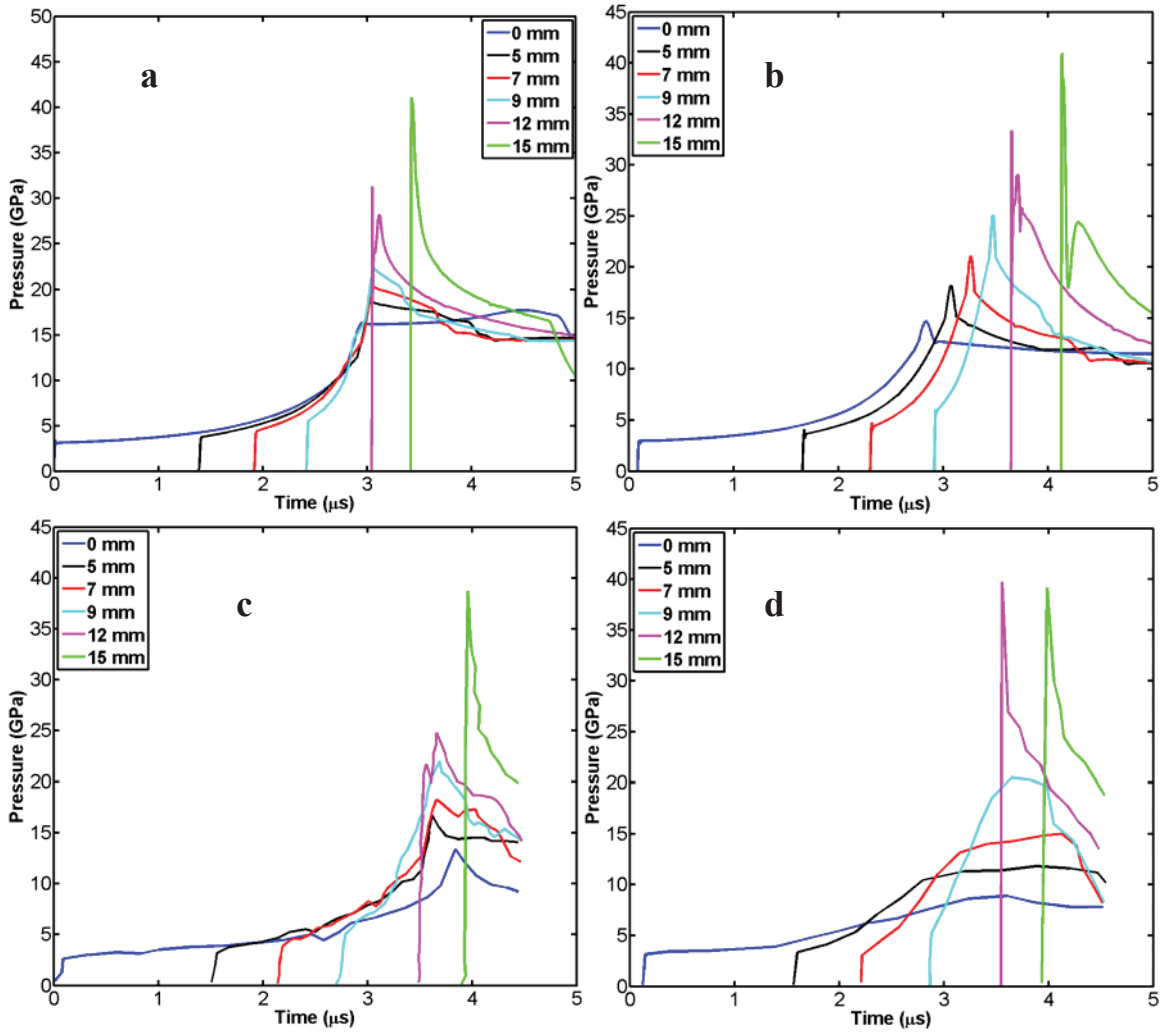

FIGURE 4. Comparison of SPH using original EoSs, fitted EoSs, FVM and experiment. Impact pressure is 3.4 GPa. Ambient temperature is 25 ºC. (a) Simulation of SPH using original EoSs; (b) Simulation of SPH using fitted EoSs; (c) Simulation of FVM using original EoSs; (d) Experiment.

The velocity *Vx* is set to be 480 m/s, and the impact pressure is around 3.4 GPa. The comparison of SPH using original EoSs, fitted EoSs, FVM [7] and experiment [7] is shown in Fig. 4. It can be seen from Fig. 4(b) that the calculated arrival time of shock wave is very close to experiment. The peak pressure calculated from fitted EoS is around 40 GPa, which also coincides well with experiment. However, all three simulations deviate from experiment somehow. It probably results from three reasons: first, detonation of high explosive is very complicated problem, even if ignition and growth model can accurately predict arrival time, peak pressure, and rough build-up process of shock wave, it can not accurately describe every detail of pressure history; second, the boundary conditions of the numerical model is simplified compared with experiment; third, the model is 1D, which is different from the 3D experiment in reality.

CONCLUSION

EoS plays fundamental role in numerical models for high explosives. Traditionally, EoS can only be obtained through experiment, which is not only costly but also dangerous. The paper presents a method to calculate EoS of solid and gaseous products of β−HMX using a series of NVT molecular dynamics simulation. Then, the calculated EoSs are applied in our in-house smooth particle hydrodynamics codes. The simulation using fitted EoSs is compared with experiment and results obtained by other numerical methods. It is found that the SPH using fitted EoSs can well predict arrival time and peak pressure in some cases. However, due to the complexity of detonation problems, all numerical models can not well predict details of pressure history, though they can roughly describe the build-up process. Other reasons for the error are probably: first, the boundary conditions of the numerical model are simplified compared with experiment; second, the numerical model is in 1D, which is different from experiment in reality.

It is concluded that though ignition and growth model is complex model with reasonable physical assumptions, it is still far from a perfect model. Molecular dynamics simulation provides a good choice to calculate EoSs of solid and gaseous products of high explosives besides field experiment.

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