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Toward a Thermal Disequilibrium Multiphase Model for High Explosives Containing Metallic Particles

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To investigate the effects of explosive composition on Al combustion, in particular regarding its oxygen balance, several liquid mixtures are experimentally studied with varying oxygen balance. They are then loaded with Al particles and the velocity of detonation (VOD) is recorded. Computational results with the help of conventional Chapman Jouguet (CJ) codes are compared but fail to reproduce experimental observations. A new multiphase flow model out of thermal equilibrium is then considered. Two options are considered as limiting cases: stiff thermal relaxation and vanishing heat exchange between Al and detonation products. With this last option, predictions

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are in excellent agreement with the experiments. This suggests that temperature disequilibrium plays a major role in heterogeneous explosives detonation dynamics.

Keywords: detonation waves, heterogeneous explosives, high explosives, multiphase flows, nonideal explosives

Introduction

Metallic particles and in particular aluminum (Al) are known for their capabilities to enhance propulsive effects of energetic materials. Their effects on detonation dynamics are still misunderstood. In order to investigate both effects of explosive composition, in particular regarding the oxygen balance (OB) as well as particle sizes on Al combustion, experimental investigations have been conducted for mixtures of tetranitromethane (TNM), nitrobenzene (NB), and aluminum jelled by a poly(methyl methacrylate) (PMMA) additive. The experimental facility and main results have been reported in Belski et al. [1] and are summarized in the present article. To interpret these results, conventional Chapman Jouguet (CJ) codes based on thermodynamic equilibrium were used with several options. Different equations of state (EOS) were used with different parameters database and different codes, as well as different modeling options (inert Al or reactive Al in thermodynamic equilibrium). None of these computations was able to reproduce the experimentally recorded velocity of detonation (VOD) when Al particles are present. For liquid mixtures free of aluminum, the closest CJ code predictions were obtained with the Cheetah code, used with the EOS Becker-Kitiakovsky-Wilson (BKW), using Hobbs and Baer [2] calibrated parameters from a large database BKW-Sandia (BKWS). However, in the presence of aluminum, considered as inert, a defect of about 200–250 m/s was obtained in the computations, by comparison with the measured VODs. This observation was surprising, because even when the maximizing assumption of reacted Al in thermodynamic equilibrium was assumed, this VOD defect was present.

These observations gave motivations to investigate multiphase flow models in which temperature disequilibrium is considered. Indeed, most detonation wave computations with the CJ model, Zeldovich-Von Neumann-Doering model (ZND), and unsteady codes consider the reactive Euler equations. This approach assumes mechanical and thermal equilibrium among the various phases. This last assumption is valid for ideal gas mixtures but seems excessive in the context of heterogeneous explosives. In order to examine temperature nonequilibrium effects, the two-phase reduced model of Kapila et al. [3] is considered as the starting point. This model was developed to describe the deflagration-to-detonation transition in granular material for which velocity and pressure relaxation is a stiff phenomenon. This approach assumes a single pressure and single material velocity and remains out of thermal equilibrium. Petitpas et al. [4] extended this model to an arbitrary number of phases, adding heat and mass transfer, and determined generalized CJ conditions. An appropriate numerical method to solve this flow model was built by Saurel et al. [5]. The aim of this article lies in the application of this multiphase model to the computation of detonation characteristics of TNM, NB, and Al mixtures jelled by PMMA. It will be shown that the agreement between computed results and experiments is considerably improved with the temperature nonequilibrium multiphase model.

The article is organized as follows. The multiphase flow model in the presence of mass transfer is recalled in the next section. The experimental facility reported in Belski et al. [1] is then summarized. Thermodynamic closure and kinetic laws for the specific explosive mixture under interest are presented in the following section, and the final section deals with the comparison of experimental and computed results.

Multiphase Model

The aim is to compute the detonation wave propagation characteristics (detonation pressure, detonation temperature, and VOD) with a multiphase model involving as few parameters as possible. In this aim, velocity and pressure disequilibrium are

omitted and a reactive mechanical equilibrium model with several temperatures is considered. The use of such a mechanical equilibrium model is justified by analyzing mechanical and thermal relaxation timescales. The pressure and temperature relaxation timescales [4] can be approximated respectively by $\tau_P \approx d/c$ and $\tau_T \approx \frac{\rho C_V}{4\lambda} d^2$, with λ as the metallic particles' thermal conductivity, C_V their constant volume specific heat, ρ their density, c their sound speed, and d their diameter. The ratio between pressure and velocity timescales is given by the relation

$$\frac{\tau_u}{\tau_P} \approx \frac{1}{\rho} \frac{\alpha_1 \alpha_2}{c_1 c_2} \left(\frac{\rho_1 c_1^2}{\alpha_1} + \frac{\rho_2 c_2^2}{\alpha_2} \right).$$

where α represents the volume fraction. In the detonation state, the indices 1 and 2 represent respectively the detonation products and the particles. Their acoustic impedances and densities are generally of the same order of magnitude in the detonation state of condensed high explosive (HE), so that the two mechanical relaxation times are of the same order ($\frac{\tau_u}{\tau_P} \approx 1$). For the mixture TNM-NB-PMMA-Al $7 \mu\text{m}$ 39.03-27.97-3-30 used here, this ratio is 1.6 in the detonation conditions. The τ_P and τ_T relaxation time estimates are respectively 1 and 154 ns. The mechanical relaxation times are significantly lesser than the reaction time, estimated as 80 ns from the plane shock experiments on TNM-NB mixtures described later. The temperature relaxation time is larger than the chemical reaction timescale. Increasing twofold aluminum temperature leads to 332 ns for the temperature relaxation timescale because of thermal conductivity and heat capacity variations versus temperature. This timescale strongly increases with the particle diameter to attain 48 μs for 100- μm particles and becomes of the order of the reaction timescale for submicrometer particles.

For the present application, a model involving an arbitrary number of phases is preferred to a two-phase approach. Indeed, we are going to consider two instances:

- Two-phase computations involving liquid reactive mixture: Al as a single condensed phase and detonation products (DPs) plus Al in temperature equilibrium as another phase

- Three-phase computations in which the Al is considered as another phase, with its own temperature

With these two options, the two bounds of infinitely fast and infinitely slow temperature relaxation effects are considered.

Conventional models deal with the reactive Euler equations, with mixture equation of state for the condensed phase and DPs. A conventional assumption for the building of such equation of state (EOS) consists in temperature and pressure equilibrium between condensed HE and DP, which is a tedious approximation for reacting multiphase flows.

A total nonequilibrium multiphase model was developed with a new homogenization method, called the *discrete equations method* (DEM) by Abgrall and Saurel [6]. This method considers multiphase mixtures at the discrete level and accounts for phase interactions with the help of Riemann solvers, as was done originally by Godunov to solve single-phase flows. This method provides discrete equations that can be implemented directly into hydrocodes. A variant of this approach was developed by Chinnayya et al. [7] for nonideal HE-containing ammonium perchlorate, hexogen, hydroxyl-terminated-polybutadiene (HTPB) binder, and Al particles. They also determined the continuous limit of these discrete equations and recovered the Baer and Nunziato [8] model, completed by explicit relationships for the interface mechanical parameters as well as mechanical relaxation coefficients. They finally determined the asymptotic limit of this model in the presence of stiff mechanical relaxation. Doing so, the two-phase model of Kapila et al. [3] was recovered. Petitpas et al. [4] extended this last model to an arbitrary number of phases in the presence of heat and mass transfers. This model is considered here for the modeling of TNM-NB-Al mixtures detonation characteristic in order to interpret Belski et al.'s [1] experimental results.

Petitpas et al.'s [4] model is considered in the absence of heat transfer. Indeed, we are going to analyze results in two limiting cases:

- Al evolving freely, without heat exchange with the mixture.

- Al constrained by the detonation products equation of state.

These two limiting cases are of interest because precise knowledge of heat exchange coefficients under detonation conditions is an issue.

In the absence of heat transfer, Petitpas et al.'s [4] model is composed of the conventional mass, momentum, and total energy conservation equations (Euler equations),

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \text{div} \vec{v} (\rho \vec{u}) &= 0 \\ \frac{\partial (\rho \vec{u})}{\partial t} + \text{div} \vec{v} (\rho \vec{u} \otimes \vec{u}) + \text{grad} P &= 0, \\ \frac{\partial (\rho E)}{\partial t} + \text{div} ((\rho E + P)\vec{u}) &= 0 \end{aligned}$$

complemented by equations for the volume and mass fractions for each $N - 1$ phase:

$$\frac{\partial \alpha_k}{\partial t} + \text{div}(\alpha_k \vec{u}) = \frac{\rho c^2}{\rho_k c_k^2} \alpha_k \left(\text{div} \vec{u} - \sum_i \frac{\dot{m}_i}{\rho_i} \right) + \frac{\dot{m}_k}{\rho_k},$$

$$\frac{\partial (\alpha \rho)_k}{\partial t} + \text{div} ((\alpha \rho)_k \vec{u}) = \dot{m}_k \text{ or } \frac{\partial (\rho Y_k)}{\partial t} + \text{div} (\rho Y_k \vec{u}) = \dot{m}_k = \rho \dot{Y}_k.$$

The saturation constraint and the mixture mass definition impose: $\sum_k \alpha_k = 1$ and $\sum_k Y_k = 1$.

The thermodynamic closure is given by the definitions for the mixture internal energy and mixture specific volume,

$$e = \sum_k Y_k e_k(P, T_k), \quad v = \sum_k Y_k v_k(P, T_k),$$

under the pressure equilibrium constraint:

$$P = P_k = P_i \quad \forall k, i$$

The functions $e_k(P, T_k)$ and $v_k(P, T_k)$ represent the equations of state for each phase. Variables α_k , Y_k , T_k , ρ_k , and v_k represent volume fraction, mass fraction, temperature, density, and specific volume of the different phases respectively. P , e , ρ , and v represent the pressure, internal energy, density, and specific volume for the mixture, respectively.

The volume fractions equations for the $N - 1$ phases can be replaced by specific volume equations that are easier to implement in conventional Lagrangian hydrocodes:

$$\frac{dv_k}{dt} = \frac{v_k^2 c^2}{c_k^2 v^2} \left(\frac{dv}{dt} - \sum_i \dot{Y}_i v_i \right)$$

The volume fraction equations being nonconservative, nonconventional Hugoniot relations are needed to close this hyperbolic system. Approximate shock jump relations were determined in Saurel et al. [9] in the weak shocks limit:

$$\begin{aligned} Y_k^* &= Y_k^0 \\ \rho^*(u^* - D) &= \rho_0(u_0 - D) = m \\ P^* - P_0 &= m^2(v_0 - v^*) \\ e_k^* - e_k^0 &= \frac{P^* + P_0}{2}(v_k^0 - v_k^*) \end{aligned}$$

with

$$v = \sum_k Y_k v_k, \quad e = \sum_k Y_k e_k$$

The symbol $*$ denotes the shock state and the symbol 0 the initial state. These relations have been validated in the same reference against experimental data involving weak and strong shocks with various mixtures. Agreement is reported in Trunin [10], where a larger database has been studied, as well as very strong shocks.

Experimental Facility

The experimental facility of Belski et al. [1] is shown schematically in Fig. 1. The TNM-NB-PMMA-Al mixture is filled inside two steel tubes of internal diameter 29 mm and external

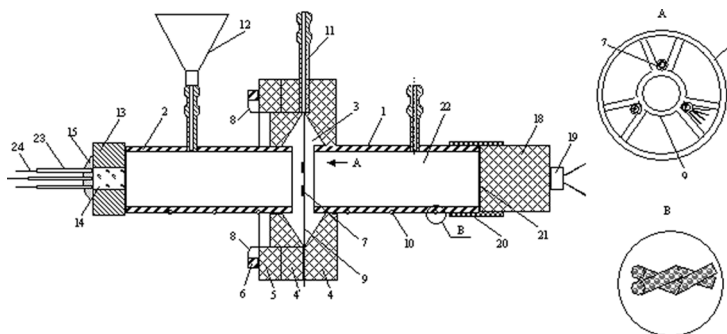


Figure 1. Experimental setup to measure the detonation characteristics: 1–2, steel pipes, inner diameter 29 mm, outer diameter 33 mm; 3, annular cavity in the plastic ring; 4, 4-ft plastic rings; 7, helix manganin gauges; 9, mica plates; 10, enameled wires to measure VOD; 13, aluminum blocks; 14, LiF window; 18, primer cylinder of HMX-based HE; 19, detonator; 20, plastic HE layer; 21, protective steel foil; 22, studied mixture, 23–24, ferules and optical fibers.

diameter 33 mm, connected by plastic rings. Each steel tube has a length of 75 mm. The annular cavity between the plastic rings is used for the pressure measurements using three bifilar helix manganin gauges (diameter 4.5 mm, thickness 0.03 mm) embedded in two mica plates of 0.15 mm thickness with holes for the liquid mixture passage when it fills the system. An HMX cylinder placed at the tube inlet is used to ignite the liquid-Al mixture through a protective steel foil. The tube end is closed by a lithium fluoride (LiF) window of size $6 \times 6 \times 15$ mm used for the DP spectral radiance measurement. The spectral radiance is collected through optical fibers and its intensity is measured using a multichannel pyrometer on wavelengths 406, 451, 498, 550, and 600 nm. Only the radiance intensity measured when the detonation front reaches the LiF window is examined. The VOD is recorded along the steel tube by electric contacts composed of enameled wires of diameter 0.1–0.2 mm connected to a resistive circuit, as shown in Fig. 2. The time intervals are measured with accuracy of 5 ns.

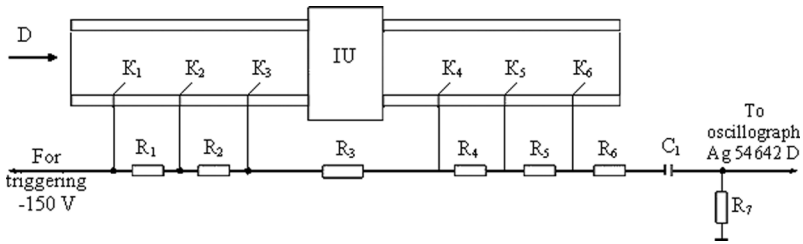


Figure 2. Resistive circuit to record the detonation wave chronometry.

Examples of the luminance temperatures recorded just after the detonation–LiF window interaction are given in Table 1 for the mixture TNM-NB-PMMA-Al 39.03-27.97-3-30% in mass. This HE composition corresponds to an OB of -39.3 for the TNM-NB liquid mixture. The thermal radiance emitted by aluminized HE detonation products is composed of the radiances emitted by the gaseous phase, the solid carbon, and the aluminum particles. It is difficult to compare these experimental data with numerical simulation because of the lack of knowledge in spectral emissivity for each DP constituent at these pressure and temperature levels. However, these data are useful for mixtures of liquids only; they represent a minimum of the DP temperature according to classical radiation model: $L_\lambda = \varepsilon(\lambda, P, T)L_0(\lambda, T)$, where L is the luminance, ε the emissivity, and λ the wavelength, as discussed in Leal-Crouzet et al. [11]. The luminance temperature is deduced from the luminance with an accuracy of 5%. Determination of

Table 1

Luminance temperature versus wavelength for TNM-NB-PMMA-Al 39.03-27.97-3-30% in mass (OB -39.3 for TNM-NB)

Wavelengths (nm)	406	450	498	550	600	Shot
Luminance temperature (K)	3,410	3,325	3,300	3,320	3,190	F14
Luminance temperature (K)	3,000	2,995	2,980	2,900	2,800	F15

the true temperature needs spectral emissivity $\varepsilon(\lambda, P, T)$ knowledge of the TNM-NB-PMMA detonation products, still an issue for the HE considered here.

Typical pressure records obtained for TNM-NB-PMMA-Al 39.03-27.97-3-30 are shown in the Results section and are compared with computed ones in Fig. 3. The detonation pressure is difficult to determine from the pressure history because of experimental errors of this type of measurement ($\sim 10\%$) and because of pressure equilibrium characteristic time of the gauge with the reactive flow. These records will thus be considered as a first estimation of the detonation pressure.

The detonation velocity is measured within an error of 0.6% taking into account the enameled wire's diameter and the repeatability errors of experiments performed for a similar HE composition. The measured VOD is $6,835 \pm 41$ m/s for TNM-NB-PMMA-Al 39.03-27.97-3-30 in a 29-mm steel tube. The effect of internal charge diameter has been studied for the composition TNM-NB-PMMA-Al 64.38-22.62-3-10. The VOD is $7,484 \pm 45$ m/s with a 29-mm-diameter tube and $7,448 \pm 45$ m/s with a 57-mm-diameter tube. The difference in the measurement error bar, the VOD recorded in 29 mm

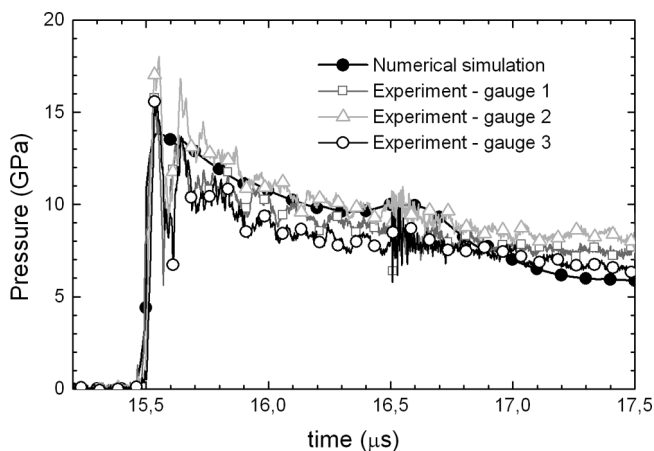


Figure 3. Pressure histories for TNM-NB-PMMA-Al 39.03-27.97-3-30% in mass (OB -39.3 for TNM-NB).

diameter, can be considered as a CJ VOD corresponding to a plane steady detonation wave.

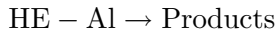
Equations of State and Chemical Kinetic Relations

The equations of state and chemical kinetic models are now presented for flow model application to a TNM-NB-PMMA-Al HE mixture.

Two reaction models have been developed and are described below. They correspond to the two limiting cases where:

- The heat transfer rate between detonation products and Al is stiff: temperature equilibrium is assumed between the gas products and Al.
- The heat transfer rate between detonation products and Al is zero: Al evolves freely, without heat exchange.

The first option corresponds to a two-phase model; the first phase is composed of liquid explosive mixture plus Al, and the second phase is composed of the detonation products and the Al particles in thermal equilibrium. This model is based on the following one-step chemical reaction:



The HE contains TNM and NB, whose mass fractions are adjusted to obtain the desired OB plus 3% of PMMA additive. The term $\sum_i \dot{Y}_i v_i$ of the volume fraction equations thus reduces to $\sum_i \dot{Y}_i v_i = \dot{Y}_{\text{HE-Al}} (v_{\text{HE-Al}} - v_{\text{Products}})$.

The second option is a three-phase model: HE, inert Al, and the HE detonation products. This model is based on the following one-step chemical reaction:



The Al particles are in temperature nonequilibrium with both HE and detonation products. Assuming inert Al particles ($\dot{Y}_{\text{Al}} = 0$) the term $\sum_i \dot{Y}_i v_i$ in the volume fractions equations reduces to $\sum_i \dot{Y}_i v_i = \dot{Y}_{\text{HE}} (v_{\text{HE}} - v_{\text{Products}})$.

These two options consider the Al as inert. Al combustion is assumed to occur mainly in the expansion wave behind the sonic locus and is responsible for explosive ballistic efficiency only, not for detonation dynamics. A single kinetic rate describing the TNM-NB decomposition is thus needed. Its determination is addressed later.

Equations of State for Unreacted Phases

The HE mixture under study is composed of two liquids and metallic particles jelled by a few percent of PMMA. The metallic particles EOS is known up to the detonation level, but the liquid mixture EOS is unknown. In order to determine the liquid mixture Hugoniot the universal D-u shock relationship proposed by Woolfolk et al. [12] is used:

$$\frac{D}{u} = 1.62 + (1.37 - 0.37e^{-2u/C_0}) \frac{C_0}{u}$$

Figure 4 illustrates the accuracy of this relationship for several liquids in the diagram $D/u = f(C_0/u)$.

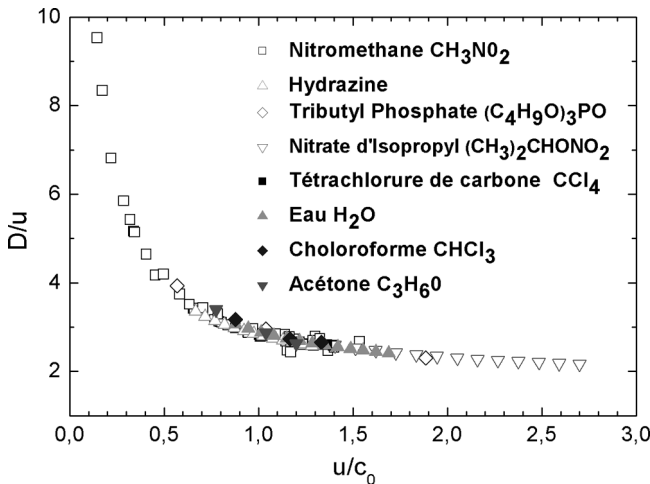


Figure 4. Accuracy of the Woolfolk et al. [12] universal D-u relationship for several liquids.

To use this model, the sound speed C_0 only is required to determine the D-u relation for TNM-NB mixtures. This sound speed is calculated with the help of Wood's relationship [13]:

$$\frac{1}{(\rho_0 C_0)^2} = \frac{Y_{\text{TNM}}}{(\rho_0 C_0)_{\text{TNM}}^2} + \frac{Y_{\text{NB}}}{(\rho_0 C_0)_{\text{NB}}^2}$$

This relation can also be deduced from the hyperbolicity analysis of our multiphase flow model [3,4] assuming that the PMMA additive contribution is small enough to be neglected.

For TNM and NB, the sound speeds are available in Zotov [14]. The various HE constituents' data, regarding sound speed, density, specific heat capacity, and enthalpy of formation, are summarized in Table 2.

Then, the TNM-NB-Al mixture shock wave data are theoretically determined using the two-phase shock-jump equations applied to the mixture of the liquid TNM-NB and Al particles. Figure 5 illustrates the results obtained for the TNM-NB-Al 41-29-30 HE composition in the D-u plane. The computed shock-jump states correspond to square point symbols and the line corresponds to the linear fitting curve ($D = 1305 + 3.107 u$ m/s), valid in the velocity range 250-2,000 m/s.

Assuming a linear D-u relationship, it is possible to determine the Cochran and Chan [15] EOS parameters:

$$P = A_1 \left(\frac{\rho}{\rho_0} \right)^{E_1} - A_2 \left(\frac{\rho}{\rho_0} \right)^{E_2} + \Gamma \rho C_v T$$

$$e = \frac{A_1}{\rho_0(E_1 - 1)} \left(\left(\frac{\rho}{\rho_0} \right)^{E_1 - 1} - 1 \right) - \frac{A_2}{\rho_0(E_2 - 1)} \times \left(\left(\frac{\rho}{\rho_0} \right)^{E_2 - 1} - 1 \right) + e_0 + C_v(T - T_0)$$

where A_1 , A_2 , E_1 , E_2 are fitted to reproduce the D-u diagram. The Gruneisen coefficient and the heat capacity C_v are assumed constants. The Cochran-Chan EOS is used for liquid HE, liquid HE-Al mixtures, and aluminum alone.

Table 2
HE constituents' data

Constituents	C_0 (m/s)	Density (g/cm ³)	C_p (cal/g)	H_f (kJ/mol)
C(NO ₂) ₄ -TNM	1,039	1.638	0.290	38.00
C ₆ H ₅ NO ₂ -NB	1,473	1.205	0.340	15.91
C ₅ H ₈ O ₂ -PMMA	2,600	1.186	1.20	430.53
Al	5,350	2.700	0.213	0

Equation of State for Detonation Products

The HE and HE-Al detonation products are described by a Jones-Wilkins-Lee (JWL) EOS theoretically determined for each composition using thermochemical computations. Various different thermochemical codes (Cheetah 2.0 [16], QUERCY [17], MIROQ [18]) and various EOS (BKW, Jacobs-Cowperthwaite-Zwisler JCZ3, Exp-6 Buckingham, Blake, H9 Virial expansion with QUERCY and MIROQ) with several sets of parameters for the gaseous species have been tested to assess their accuracy to model VOD of TNM-NB-PMMA mixtures.

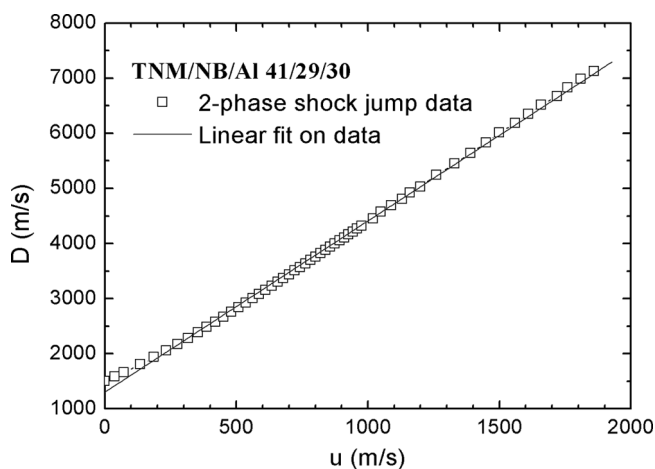


Figure 5. 41/29/30 TNM/NB/Al mixture D-u relationship.

Table 3
 Calculations of the velocity of detonation for TNM-NB-PMMA 71.78-25.22-3 (OB -6% for TNM-NB) using the EOS JCZ-Sandia (JCZS), Buckingham Exp6, New C1, BKW-Cheetah (BKWC), BKW-Sandia (BKWS) and Blake with Cheetah 2.0 and H9 Virial expansion with QUERCY and MIROQ

	Experiment	Cheetah JCZS small	Cheetah JCZS	Cheetah Exp-6 Buckingham	Cheetah new C1
P_{CJ} (GPa)	≈ 19	20.58	20.58	20.93	22.30
T_{CJ} (K)	$> 4,385$	5,160	5,155	5,002	4,733
D_{CJ} (m/s)	$7,516 \pm 45$	7,313	7,312	7,618	7,466
Code/EOS	Cheetah BKWC	Cheetah BKWS	Cheetah Blake	QUERCY H9 Baudin	MIROQ H9 Heuze
P_{CJ} (GPa)	21.60	22.64	17.81	18.54	18.29
T_{CJ} (K)	5,075	5,312	5,611	4,536	4,548
D_{CJ} (m/s)	7,777	7,509	5,277	6,969	6,923

Their predictions are compared in Table 3 against the experimental data of Belski et al. [1] for a mixture of TNM-NB of oxygen balance -6% plus 3% of PMMA additive (TNM-NB-PMMA 71.78-25.22-3% in mass). These experimental data correspond to the recorded VOD, detonation pressure, and luminance temperatures. Here, the PMMA additive cannot be neglected in thermochemical computations because of its large negative oxygen balance: adding 3% of PMMA in a TNM-NB OB -6% leads to a global oxygen balance of -11% . The PMMA additive will take into account in all thermochemical computations.

The Cheetah 2.0 code used with BKWS (EOS BKW with Hobbs and Baer database [2]) gives the best results. It accurately predicts pressure and VOD ($7,509\text{ m/s}$ compared to the experimental data $7,516 \pm 45\text{ m/s}$ for TNM-NB OB -6% 97/PMMA 3). Thus, all computations in the Results section will be done with the JWL parameters fitted under CJ computations using BKWS as an option for HE alone as well as for HE-inert Al.

The JWL EOS reads:

$$\begin{aligned}
 P(\rho, e) &= A \left(1 - \frac{\omega}{R_1} \frac{\rho}{\rho_0} \right) e^{-R_1 \frac{e_0}{\rho}} \\
 &\quad + B \left(1 - \frac{\omega}{R_2} \frac{\rho}{\rho_0} \right) e^{-R_2 \frac{e_0}{\rho}} + \omega \rho e, \\
 T &= T_S(\rho) + \frac{P - P_S(\rho)}{\omega \rho C_V}
 \end{aligned}$$

$P_S(\rho)$ and $T_S(\rho)$ represent the pressure and the temperature along the CJ isentrope. They are given by:

$$P_S(\rho) = A e^{-R_1 \frac{e_0}{\rho}} + B e^{-R_2 \frac{e_0}{\rho}} + C \left(\frac{\rho}{\rho_0} \right)^{\omega+1} \quad \text{and} \quad T_S(\rho) = T_{CJ} \left(\frac{\rho}{\rho_{CJ}} \right)^{\omega}.$$

The Gruneisen coefficient ω and the heat capacity C_V are assumed constants. The parameters A , B , C , R_1 , R_2 , and ω are fitted to reproduce the CJ isentrope and the CJ conditions. The heat capacity is evaluated at CJ state.

Chemical Decomposition Rate

The TNM-NB liquid mixture reaction rate ($\frac{dY_1}{dt} = \dot{Y}_1$) is calculated using a conventional reaction model for liquid energetic materials,

$$\dot{Y}_1 = -Y_1 k(T_1),$$

where Y_1 is the reaction progress variable (here the mass fraction of phase 1) and $k(T_1)$ a function of the HE or HE-Al temperature calculated using the Cochran-Chan equation of state. The subscript 1 denotes TNM-NB-PMMA-Al in the two-phase model and TNM-NB-PMMA in the three-phase model.

The reaction rate temperature dependence $k(T_1)$ is modeled by the Arrhenius law:

$$k(T_1) = A \exp\left(-\frac{T_{\text{act}}}{T_1}\right)$$

The preexponential factor A and the activation temperature T_{act} are determined to reproduce shock-to-detonation (SDT) experimental data at high pressure.

Figure 6 represents the experimental setup developed by Leal-Crouzet et al. [19] for Arrhenius parameters determination. A powder gun is used to accelerate a plane copper plate in the range 850–2,300 m/s to impact a TNM-NB cell. This cell is composed of a copper transfer plate and a polyethylene cylindrical box. The cell is filled with TNM-NB mixture; its internal depth is 4 mm. Piezoelectric pins record the copper plate velocity and the material velocity inside the TNM-NB mixture. An optical head connected to an optical UV-Vis spectrometer records the thermal radiance emitted by the TNM-NB reactions during SDT.

Thermal radiance signals for several wavelengths are shown in the Fig. 7 for a TNM-NB 65–35 in volume (71.63–28.27 in mass) corresponding to an OB of –11%. This OB was selected to correspond to the TNM-NB OB –6% plus 3% of PMMA mixture used at VNIIEF. The cell containing the explosive

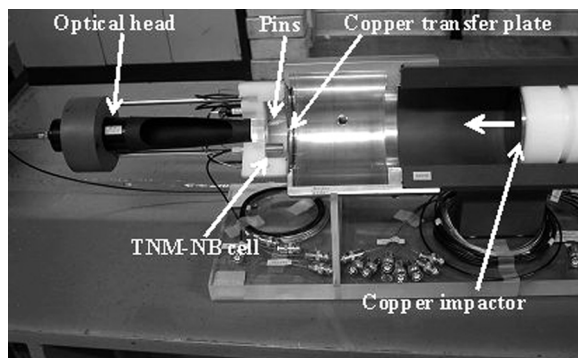


Figure 6. Photograph of TNM-NB shock initiation experiments.

mixture is impacted at 1,934 m/s. The detectors 1 and 2, at wavelength 811 and 778 nm, exhibit the classical behavior of liquid explosives SDT: the formation of a superdetonation after an induction time (detonation propagating inside the shock compressed TNM-NB mixture) and the formation of an overdriven detonation when the superdetonation reaches the initial shock wave. The reaction induction time is about 35 ns and the detonation formation appears 75 ns after the shock wave

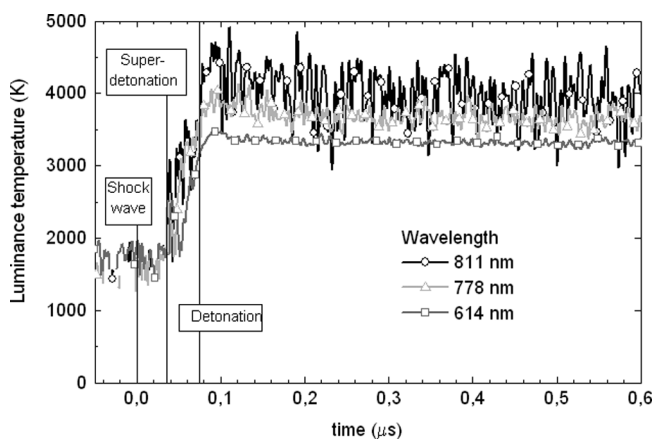


Figure 7. Thermal radiance signals for several wavelengths, recorded using the spectrometer.

emergence inside the TNM-NB mixture. Most homogeneous HEs obey a two-stage decomposition process corresponding to the induction and the recombination stages.

This process rate, during the induction period $\tau = 35$ ns, is well represented by the Arrhenius law. The induction properties can be deduced from the reaction rate and the reactive flow equations by a procedure proposed by Vidal and Khasainov [20] for arbitrary shock dynamics. The framework of this procedure is the formal Cauchy problem for quasihyperbolic first-order differential equations. Applied to detonation impact, the induction time is related to (A, T_{act}) activation parameters coupled through the relation:

$$\tau = \frac{T_S}{T_{\text{act}}} \left(\frac{1}{T} \frac{dT}{dt} \right)_S^{-1}$$

where

$$\frac{1}{T} \frac{dT}{dt} = \frac{\Gamma}{\rho c^2} \frac{dP}{dt} - \frac{Q_{PT}}{C_P T} \dot{Y}_1 = \Gamma \rho \frac{dv}{dt} - \frac{Q_{VT}}{C_V T} \dot{Y}_1$$

The magnitude of the ratios $\frac{T_{\text{act}}}{T_S}$ and $\left(\frac{1}{T} \frac{dT}{dt} \right)_S$ in the initial induction state (where the subscript S means the shock state) measures the rate sensitivity. $\frac{Q_{PT}}{C_P}$ and $\frac{Q_{VT}}{C_V}$ are respectively the adiabatic explosion temperatures at constant pressure and constant volume. Γ is the Gruneisen coefficient. Considering constant volume conversion,

$$\left(\frac{1}{T} \frac{dT}{dt} \right)_S = \frac{Q_{VT}}{C_V T_S} A \exp\left(-\frac{T_{\text{act}}}{T_S}\right) \quad \text{and}$$

$$\tau = \frac{T_S}{T_{\text{act}}} \frac{C_V T_S}{Q_{VT}} \frac{1}{A} \exp\left(\frac{T_{\text{act}}}{T_S}\right)$$

Following Zotov [14], these parameters are considered to be independent of the TNM-NB mixtures oxygen balance. The parameters giving both induction time and time to detonation are selected by comparing experiments and 1D numerical computations. From Fig. 7 we obtained $A = 9.5 \cdot 10^{11} \text{ s}^{-1}$ and $T_{\text{act}} = 15,000 \text{ K}$.

Results and Discussion

The preceding multiphase flow model with associated EOS and kinetic relation has been coded in 1D Lagrangian and 2D Eulerian hydrocodes with the method developed in Saurel et al. [5]. The correct partition of the energies among the various phases for a correct determination of the various temperatures has been achieved with the correction given in Petitpas et al. [4]. The configuration under study corresponds to Belski et al.'s [1] experiments. The initial configuration and examples of 2D computations are given in the Fig. 8.

The detonation characteristics calculated for TNM-NB-PMMA-Al 39.03-27.97-3-30% in mass are given in Table 4. This mixture corresponds to a -39.3% oxygen balance for TNM-NB (oxygen balance of nitromethane). The mean diameter of Al particles is $7\ \mu\text{m}$ with purity better than 98% in mass. The calculations are performed with the JWL equation of state determined using the BKWC and BKWS databases. Four types of simulation are compared in this table: (1) an equilibrium Cheetah 2.0 calculation (line 1), (2) a 1D two-phase calculation (line 2), (3) a 2D two-phase calculation (line 3), and (4) a 1D three-phase calculation (line 4). The experimental VOD is given in line 5. The 1D two-phase numerical simulation recovers the Cheetah 2.0-computed VOD: Al particles and detonation products are in thermal equilibrium in both models. The 2D two-phase simulation leads to a VOD $38\text{--}39\ \text{m/s}$ less than the value given by 1D two-phase simulation. This difference lies within the measurement errors and leads to conclude that 1D numerical simulations are sufficiently accurate to examine the effects of thermal disequilibrium on the detonation velocity. The temperatures given in Table 4 are the computed temperatures at the sonic locus in the reaction zone. Typical temperature profiles are given in Petitpas et al. [4]. They cannot be compared with the temperature measurements, because of the spectral emission lack of knowledge. The recorded pressure histories are given in Fig. 3 and compared against the corresponding three-phase numerical simulation. The numerical results lie within the experimental data.

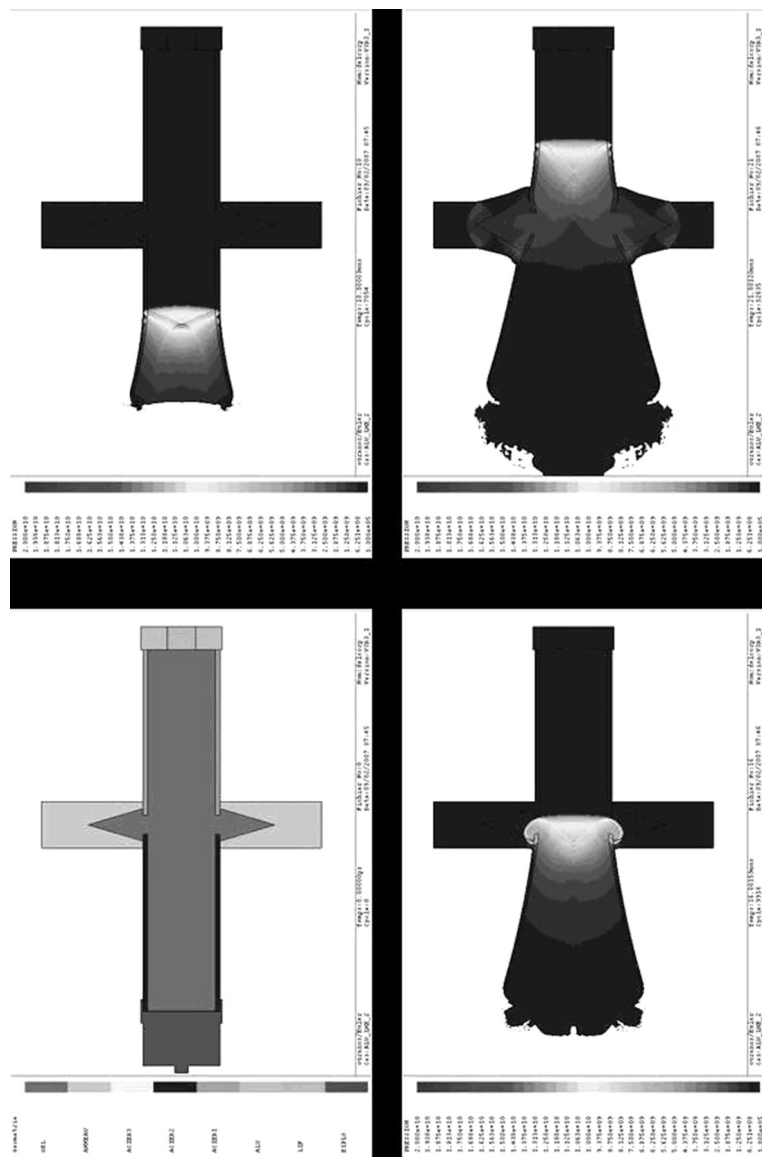


Figure 8. Numerical simulations of Belksi et al.'s [1] experiments.

Table 4
Velocity of detonation and detonation temperature of TNM-NB-PMMA-Al
39.03-27.97-3-30% in mass (OB -39.3 for TNM-NB)

	Velocity of detonation (m/s)		Detonation temperatures (K)	
	BKWC	BKWS	BKWC	BKWS
CJ DP-Al temperature equilibrium (Cheetah 2.0 calculation)	6,532	6,575	3,192	3,244
ZND Two-phase model: 1D simulation TNM-NB-Al → products (Al inert)	6,527	6,569	3,180	3,240
Curved Two-phase model: 2D simulation ZND TNM-NB-Al → products (Al inert)	6,489	6,530	3,140	3,205
Three-phase model: 1D simulation TNM-NB + Al(i) → products + Al(i) Experiment	6,780	6,795	Gas: 4,250 Al: 465	Gas: 4,300 Al: 470 >3,410

The three-phase model gives values 220–248 m/s greater than the detonation velocities obtained with the temperature equilibrium model (equilibrium between inert Al and detonation products). The best approximation of the experiment is obtained by this three-phase model (6,780–6,795 m/s compared to 6,830 m/s). Similar results have been obtained for TNM-NB oxygen balances of -30 , -20 , -6 , and $+10\%$ with 10% Al in mass, as shown in Fig. 9. The effects of temperature disequilibrium between Al particles and detonation products led to high fidelity in the computed results and can explain the differences between the experimental data and Cheetah calculations where an equilibrium temperature is assumed in all detonation products.

In order to evaluate the effects of a thermal equilibration, VOD have been measured for TNM-NB mixtures with aluminum nanoparticles encapsulated in an $\text{Si}(\text{CH}_3)_3$ layer, whose mean diameter is 100 nm. The encapsulation process, performed at the Semenov Institute at Moscow, consequently reduced the alumina formation at the surface of the particles. The purity of aluminum is better than 97% in mass. The role of $\text{Si}(\text{CH}_3)_3$ layer is also to avoid particle agglomeration. For oxygen balance less than -20% , the measured VOD lies

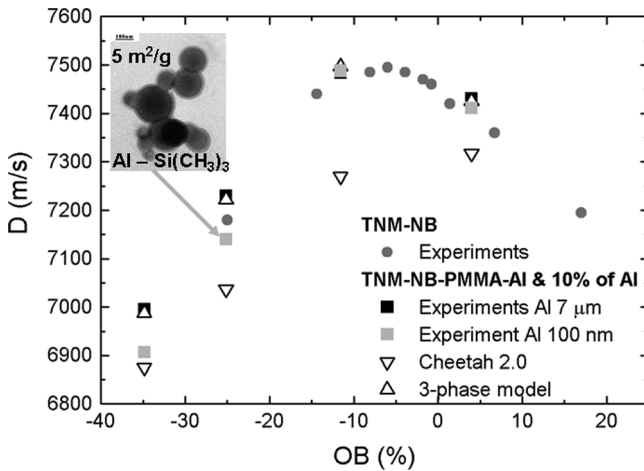


Figure 9. Velocity of detonation versus of TNM-NB-PMMA OB.

between the Cheetah calculations at thermal equilibrium (with inert Al) and the preceding experiments (Fig. 9). For oxygen balance greater than -11% , computed results and experiments are again in excellent agreement.

Conclusion

This article gives validation arguments to a recent approach for shock-to-detonation and detonation modeling in heterogeneous explosives. This approach is based on two-phase and three-phase flow models for mixtures in mechanical equilibrium but in thermal disequilibrium.

In the present work, combustion of metallic particles is not considered. Such a model is sufficiently accurate to predict the velocity of detonation and the detonation pressure, because metal combustion occurs mainly in the expansion wave behind the sonic locus, due to its slow reaction rate. The model has been applied to tetranitromethane, nitrobenzene, PMMA, and aluminum mixtures. Temperature nonequilibrium effects between Al particles and detonation products are a possible interpretation of the difference between Cheetah and experimental detonation velocities.

The main perspective is to develop a three-phase model including aluminum combustion and heat transfer to completely describe the detonation propagation and the expansion wave. At this stage of modeling, it is clear that such a model can be used for solid high explosives shock-to-detonation transition. For classical trinitrotoluene-, octogen-, hexogen-, and triaminonitrobenzene-based high explosives, a two-phase model would be sufficient. The advantage of the present approach is the extension to an arbitrary number of phases, a feature that is important for nonideal high explosives containing several components exhibiting different reaction rates.

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