

NOVEL APPROACH TO MAKE HUGONIOT PREDICTIONS: QUANTUM MECHANICS/ MOLECULAR DYNAMICS CALCULATIONS

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Abstract

This paper proposes a novel approach to predict Hugoniot properties to characterise explosives materials. The originality and uniqueness of the approach consists in using together quantum mechanics, molecular dynamics calculations combined with known analytical methods. Indeed, four well experimentally characterised energetic materials, cyclotrimethylenetrinitramine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), pentaerythritol tetranitrate (PETN) and triamino-trinitrobenzene (TATB), were investigated using quantum mechanics calculations and analytical methods. Using the pressure p and the ratio of specific densities v/v_0 , the p - v Hugoniot diagrams were obtained. Detonation velocities, D , were determined and used to define the Raleigh line. For the four compounds, the ratio of specific heats γ , a value between 2 and 3, was obtained. The γ effect, in terms of sensitivity and importance, was demonstrated. At the Chapman-Jouguet (CJ) state, the parameters (shock, particle and detonation velocities, CJ pressure and density, ratio of specific heats and Hugoniot diagrams) were predicted and all compared quite well with the published experimental data. Moreover, molecular dynamics simulations were carried out to obtain the compression p - v diagrams. Using the isothermal-isobaric ensemble (NPT), molecular dynamics simulations were conducted at various pressures ranging from 2 GPa to 40 GPa with progressive increments of 2 GPa. The Rankine-Hugoniot jump conditions were considered, the associated shock speed, U_s , and particle velocity, u_p , for each pressure, p , and relative volumetric change, v/v_0 , were calculated. The simulations showed that a linear behaviour exists between U_s and u_p for the four explosives investigated.

KEY WORDS: Hugoniot, Chapman-Jouguet, Quantum mechanics, Energetic Materials, Molecular Dynamics, Politzer

1.Introduction

Studying ignition and combustion processes of explosives including their resulting reacted (released gas products) and/or unreacted compounds (released solid products) represent significant hurdles. Extensive experimental and theoretical efforts have been made to untangle the complexity of various chemical and physical reactions that occur during the conversion of explosives into their final products, as it was pointed out by Sorescu, Rice and Thompson "[\(Sorescu et al., 1999\)](#)". These efforts remain a challenging task since a detonation is a reaction wave that takes place through a material at supersonic speed, and its temporal and spatial regime is at the nanoscale. The speed and length scale of reactions, multiple concurrent chemical and physical processes and extreme energies as well as pressures released during the events severely restrict the possibilities to carry out accurate experimental investigations.

To better design energetic materials and predict their energy output and response, it is nevertheless necessary to characterise these materials in terms of their detonation and combustion energetics. Indeed, experimental characterisation includes experiments ranging from slow cook off of materials to high velocity flyer plate impact tests. Parameters such as the detonation velocity (one of the key performance parameters of explosives), density, shock and particle velocities, and critical pressure can be obtained experimentally "[\(Cowperthwaite and Zwisler, 1973\)](#); [Cramer, 2004](#); [Fried et al., 1998](#); [Mader, 2008](#)". From these parameters, the Chapman-Jouguet point (CJ) at which a detonation occurs can be determined. This point CJ corresponds to conditions in which a detonation wave propagates with a speed that allows gaseous products to reach a sonic velocity once the reaction ends "[\(Cooper, 1996\)](#)". Pressure-specific and volume relationships called the Hugoniot curve are also among the main analytical tools to understand and compare energetic materials performance "[\(Cooper, 1996\)](#)".

The use of analytical approaches to determine the detonation parameters require *a priori* knowledge of the heat of formation ΔH_f and density of energetic materials at various pressures "([Keshavarz et al., 2014](#); [Stine, 1990](#))". Quantum mechanics calculations (QM) and molecular dynamics simulations (MD) allow estimating these parameters without having to proceed to expensive, dangerous and time-consuming experiments. For predictions of small molecule heats of formation and geometrical parameters, QM methods are considered a reliable and powerful approach. MD calculations, on the other hand, are appropriate to simulate the temporal evolution of positions and linear momentum of an ensemble of atoms or molecules subjected to a forcing function such as a shock load. As a result, molecular dynamics simulations can provide atomic-level details that cannot be obtained through measurement or use of continuum-type detonation models. MD of energetic materials has been well described in many reviews and books "([Rice and Hare, 2002](#); [Rice et al., 1999](#); [Sorescu et al., 1999](#))". It can be used to investigate changes in density with pressure, and can further allow simulations of various explosive configurations (amorphous or crystalline, different crystal polymorphs, crystals morphology, as described by the occurrence of surfaces with well-defined Miller indices). This information allow to assess the validity of assumptions used in the higher-level multiphase models proposed for initiation and detonation through a better understanding of the fundamental physics of processes occurring at the molecular level.

The work described in this paper pulls together QM, MD and analytical methods at their current state of maturity and examines to what extent these can be used in predicting and characterising the response of explosives. For this work, four well known and experimentally characterised energetic materials were used, and results are compared with documented experimental values. The four selected compounds are cyclotrimethylenetrinitramine (RDX), octahydro-1,3,5,7-

tetranitro-1,3,5,7-tetrazocine (HMX), pentaerythritol tetranitrate (PETN) and triamino-trinitrobenzene (TATB). The main objective of this present work is to determine to what accuracy the parameters that define detonation can be predicted and attempt to establish as much as possible a completely numerical approach to their estimation.

2. Methodology Details

Optimized energies and geometrical structures of the energetic compounds were calculated using the Density Functional Theory (DFT) methods "[\(Parr and Weitao, 1989\)](#)" implemented in Gaussian 09 "[\(Frisch et al., 2003\)](#)". The B3LYP hybrid functional "[\(Becke, 1988; Lee et al., 1988; Miehlich et al., 1989\)](#)" has been used in conjunction with the 6-311++G(3d,3p) basis set. The choice of the B3LYP hybrid functional was based on the fact that this functional has demonstrated to provide accurate results, comparable to those obtained by sophisticated ab initio methods, for some specific applications. For instance, the B3LYP was first developed to determine vibrational absorption spectra and circular dichroism "[\(Stephens et al., 1994\)](#)", and has been shown to be successful in predictions of heats of formation for CHNO organic molecules "[\(Tirado-Rives and Jorgensen, 2008\)](#)". In general, DFT methods are less time consuming whatever the functional used. In this study, solid state heats of formation were determined using Hess's law "[\(Atkins, 1982\)](#)" given by the expression:

$$\Delta_f H_{Solid}^0 = \Delta_f H_{Gas}^0 - \Delta H_{Sub} \quad (1)$$

where $\Delta_f H_{Gas}^0$ is the heat of formation in the gas phase, which can be predicted by using the isodesmic reaction approach "[\(Cramer, 2004\)](#)". This approach relies on experimentally known enthalpies of reaction, and derives values which are not available experimentally by finding a reaction in which the compound to be determined figures along with compounds of known

values, and in which the number of electron pairs and the chemical bond types are conserved. A moderate level of ab initio calculations, combined with the cancellation of correlation effects is invoked to explain the high accuracy observed for this approach "([Curtiss and Pople, 1999](#))".

The heat of sublimation ΔH_{Sub} was estimated using the Politzer approach "([Politzer and Murray, 2002](#))". Statistical statement is considered in this empirical approach, which assumes that various parameters characterising the materials are mapped onto isodensity surfaces of the isolated gaseous molecule of the material, and proposes the following empirical expression to calculate the heat of sublimation of materials:

$$\Delta H_{Sub} = \beta_1 A^2 + \beta_2 (v\sigma_{tot}^2)^{0.5} + \beta_3 \quad (2)$$

where A is the molecular surface area of the isolated molecule where 97% of the electron density is collected, and v defines the balance value for the positive and the negative electrostatic potential quantities on the molecular surface A of the molecule. The variance $\sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2$ defines the electrostatic potential values on the molecular surface, which is a function of the variances of the positive (σ_+^2) and negative (σ_-^2) electrostatic potentials on the surface of isolated molecule. The fit parameters are computed from a least-square fitting technique and defined as β_1 , β_2 and β_3 .

To determine the detonation velocity D , the method proposed by Stine "([Stine, 1990](#))" was used. This method may be useful for qualitative estimates of detonation velocity "([Jaidann et al., 2010](#))". The Rayleigh line and Hugoniot curve of gaseous products were obtained using the theory discussed by Fickett and Davis "([Fickett and Davis, 2000](#))". This model proposed assumes that the chemical reaction process is complete and the combustion products are instantaneously produced. The conservation of mass, momentum and energy equations are used and gas reaction products are assumed to behave as ideal gases.

Chemical structures of the four energetic molecules under study, RDX, HMX, PETN and TATB, are illustrated in Figure 1.

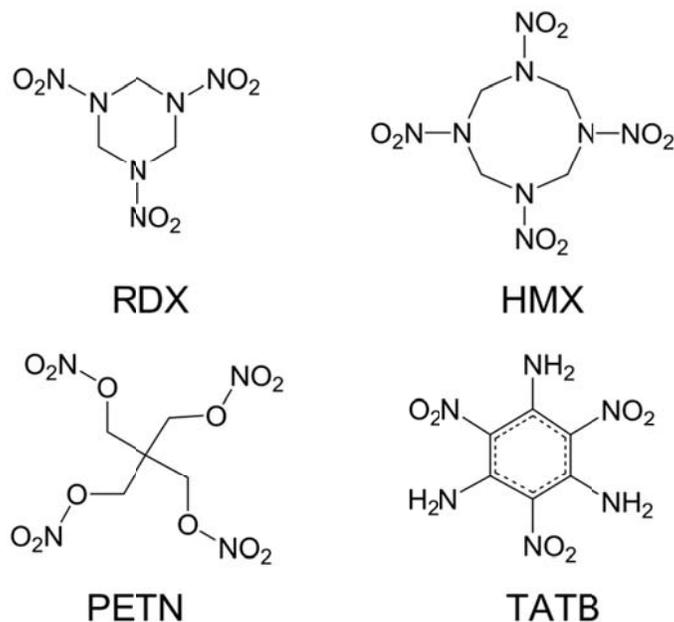


Figure 1. Chemical structure of molecules studied

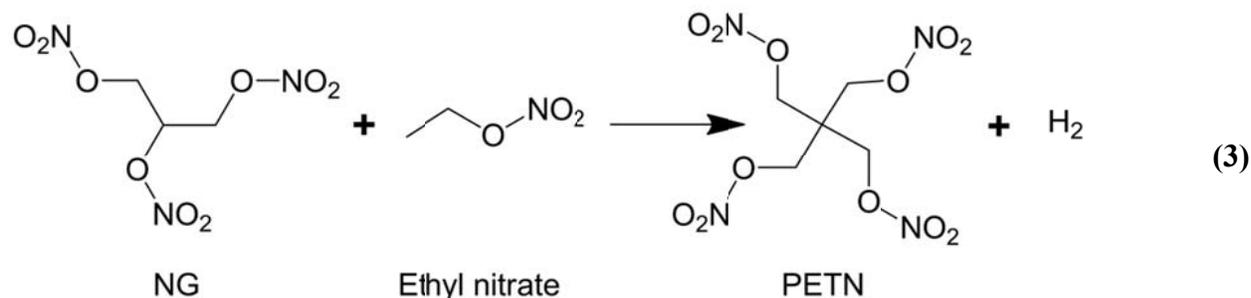
For non-reacting processes, MD simulations were carried out to determine the Hugoniot properties for the four explosives. A periodic MD simulation cell composed of a $4 \times 4 \times 4$ array of the initial crystal cell was used for these materials. Crystallographic data files of these explosives were obtained via the Cambridge Crystallographic Data Center web site ("www.ccdc.cam.ac.uk/data_request/cif"). Experimental data shows that PETN exists in two different crystalline phases, which are the tetragonal "[Trotter, 1963](#)" and orthorhombic "[Cady and Larson, 1975](#)" phases. In the current study, only the tetragonal phase, which crystallizes in the $P\bar{4}2_1c$ space group, was considered. This form is more stable than the orthorhombic phase according to Sorescu et al. "[Sorescu et al., 1999](#)". RDX and HMX also show polymorphism "[Miller and Garroway, 2001](#)". α -RDX (Pbca) and β -HMX ($P2_1/c$) crystalline phases were chosen for this study "[Cady and Smith, 1962](#); [Miller and Garroway,](#)

2001)" using the same criteria of energetic stability.

3.Result, analyses and discussions

3.1 Reacted processes of materials

As it was mentioned above, two aspects of investigations were considered in this work, one regarding the processes related to the reacted materials and another for unreacted materials. For reacted materials, quantum mechanics calculations were performed to compute heats of formation of reactants and products in the gas phase while the Politzer approach was used to estimate heats of sublimation. In the present paper, the PETN molecule is presented as an example for these calculations. The heat of formation in the gas phase of PETN was estimated using the isodesmic reaction approach shown in equation (3).



The heat of reaction is given by:

$$\Delta H_{rxn} = (\Delta_f H_{Gas,PETN}^0 + \Delta_f H_{Gas,H_2}^0) - (\Delta_f H_{Gas,NG}^0 + \Delta_f H_{Gas,Ethyl\ nitrate}^0) \quad (4)$$

Using the experimental heats of formation available on the NIST website ("www.webbook.nist.gov/chemistry"), as listed in Table 1, the PETN heat of formation can be calculated from equation (4) and will then allow calculation of the heat of formation in the gas phase using equation (5):

$$\Delta_f H_{Gas,PETN} = \Delta H_{rxn} + \Delta_f H_{Gas,NG} + \Delta_f H_{Gas,Ethyl\ nitrate} - \Delta_f H_{Gas,H_2} \quad (5)$$

Table 1. Experimental heats of formation in the gas phase of molecules in equation (3)

Molecule	$\Delta_f H_{\text{Gas}}$, kcal/mol
Nitroglycerine (NG)	-67
Ethyl nitrate	-37
PETN	-86
Hydrogen (H ₂)	0

The PETN molecule is taken here as an example to demonstrate the Politzer approach to determine the heat of sublimation. Table 2 lists the descriptor molecules used to compute β_1 , β_2 and β_3 fit parameters of equation (2). These descriptor molecules chemical compositions similar to that of PETN. The choice of a large set of CHNO descriptor molecules and similar functional groups is made to reduce the charge distribution gap between descriptor molecules and the molecule of interest, which here is PETN. The use of such an approach, by many authors "[\(Politzer et al., 2004; Rice et al., 1999\)](#)", for qualitative assessments has demonstrated its validity. It is especially useful in the field of energetic molecules, for which hazardous risks surrounding the handling of explosives in laboratories are such that the evaluation of energetic performance prior to experiments is highly desirable and recommended.

Heats of sublimation ΔH_{Sub} were estimated by the Politzer's approach, and available experimental values ΔH_{Sub} were taken from the NIST website of the descriptor molecules used in the fit. Politzer parameters shown in equation (2), A , v and σ_{total} , are reported in Table 2. Figure 2 shows the plot of predicted ΔH_{Sub} values for the selected descriptor molecules. The curve shows a satisfactory correlation between predicted and measured data. The fitting procedure and sensitivity analyses lead to fit parameters; $\beta_1 = 2.27 \times 10^{-4}$ kcal/mol.Å⁴, $\beta_2 = 2.11$, and $\beta_3 = -3.78 \times 10^{-2}$ kcal/mol. Introducing these parameters in equation (2) leads to the

estimation of a PETN heat sublimation ΔH_{Sub} of 26.85 kcal/mol with an average deviation of 0.74 kcal/mol. Equation (1) is used to determine the heat of formation in the solid phase of PETN, which is estimated to be -113 kcal/mol. The experimental value reported in the literature "[\(Ornellas et al., 1966\)](#)" is -128 kcal/mol. The relative error between the two values is around 12%, and it would likely be reduced by using accurate QM methods with a large base-set as well as an accurate model to compute the heat of sublimation, rather than the empirical approach of Politzer. As mentioned above, the objective here is to provide a helpful qualitative tool for predictions of energetic performance for explosives prior to experiments, in order to avoid unnecessary investigations of a large set of energetic materials and investing efforts only on the most worthy molecules.

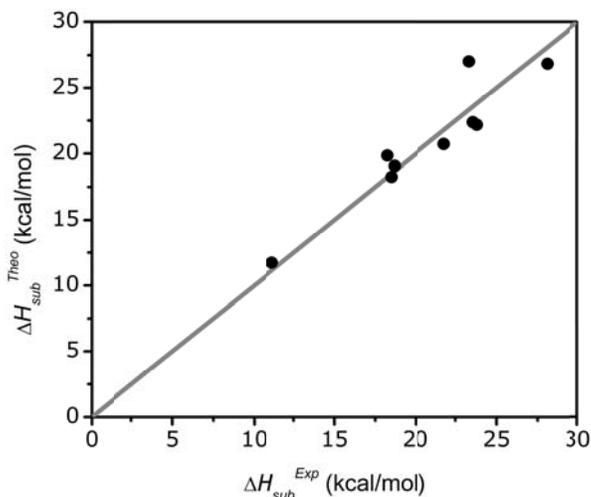


Figure 2. Predicted heats of sublimation versus experimental values of selected molecules

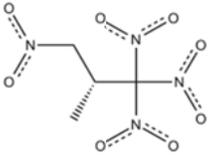
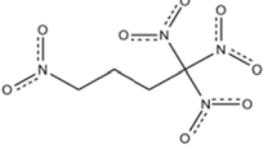
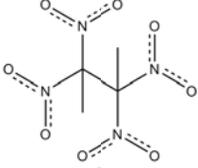
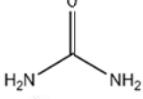
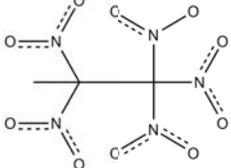
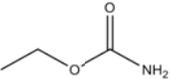
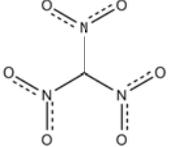
3.2 Determination of detonation velocities

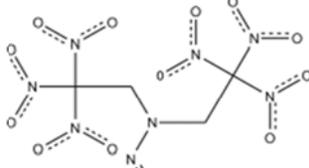
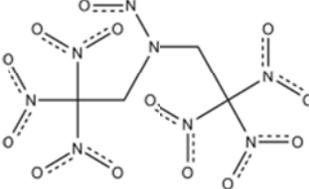
Determination of the detonation velocity D is based on the knowledge of the heat of formation in the solid phase and density, using the empirical method proposed by Stine "[\(Stine, 1990\)](#)" for a CHNO compound as described in equation (6):

$$D = D_0 + \rho \left[c_1 n_C + c_2 n_N + c_3 n_O + c_4 n_H + c_5 \Delta_f H_{Solid}^0 \right] / M \quad (6)$$

where ρ is the density and M the molecular weight of the material. D_0 is a constant, n_i , $i = C, N, O, H$, are the specific number of atoms in the molecule, c_i , $i = 1$ to 5 are the respective characteristic constants of C, N, O, H atoms (c_1, c_2, c_3, c_4), and (c_5) is the characteristic constant of the heat of formation in the solid phase of the material. D_0 and c_i constants are obtained using a least square fitting approach to equation (6). These constants are used to predict the detonation velocities of new compounds that have a chemical composition similar to that of the descriptor molecules.

Table 2. Politzer parameters of descriptor molecules for the PETN compound

Name	Chemical structure	A	v	σ_{tot}	ΔH_{Sub}
1,1,1,3-Tetranitro-2-methylpropane		235.35	0.13	10.96	91.2
1,1,1,4-Tetranitrobutane		227.32	0.11	14.96	99.6
2,2,3,3-Tetranitrobutane		204.47	0.14	12.39	78.2
Urea		95.83	0.25	19.36	98.6
1,1,1,2,2-Pentanitropropane		228.03	0.06	12.56	77.4
Ethyl carbamate		135.06	0.22	16.03	76.3
Trinitromethane		147.91	0.04	16.57	46.7

N-Nitrosobis-(2,2,2-trinitroethyl)amine		284.25	0.05	18.06	23.3
N-Nitrobis-(2,2,2-trinitroethyl)amine		295.28	0.058	13.89	24.7

The base set of explosives compounds selected to find the constants D_0 and c_i are the same five known and well characterised explosives chosen by Stine in his original work "[\(Stine, 1990\)](#)". These molecules are bis(trinitroethyl) urea (BTNEU), HMX, trinitroethyltrinitrobutyrate (TNETB), azo-bis(hexanitro) biphenyl (ABH) and ammonium picrate (Exp1D).

In order to compute the detonation velocity, D , for RDX, HMX, PETN and TATB, parameters such as the heats of formation and densities of the following molecules (ABH, BTF, BTNEU, HMX, TNETP and Exp1D) are taken from the reference "[\(Stine, 1990\)](#)" and used together with equation (6), then a least squares fitting is applied to minimise the residual sum of squares formed by the difference between calculated D values and experimental D_{exp} values. Constants D_0 and c_i ($i = 1$ to 5) obtained from the least squares fitting of equation (6) are given in Table 3.

Table 3. Comparison of D_0 and c_i parameters used by Stine and used in the present work, using the Stine method

	D_0 (km/s)	c_1	c_2	c_3	c_4	c_5
Jaidann et al. " (Jaidann et al., 2013, 2014) "	2.960	-7.039	51.586	69.034	2.214	0.463
Stine " (Stine, 1990) "	3.690	-13.850	37.740	68.110	3.950	0.691

D_0 and c_i constants used in the present work differ from those originally published by Stine. This deviation is due to the use of a more recent and optimized least square fitting algorithm, as

described in a previous in reference "[\(Jaidann et al., 2013\)](#)". The new and seemingly more accurate constants were obtained for the Stine equation. With these new constants, a better fit was found, and the estimated detonation velocities were found to be in very good agreement with experimental data.

Indeed, from Table 4, the calculated error for the detonation velocities using the new dataset is lower than that using Stine's values. For this reason, these constants are referred to as new dataset, and were used for all predictions of detonation velocities.

Table 4. Detonation velocity values: experimental D_{exp} , calculated using Stine constants (D_{Stine}) and new data proposed in this work (D in km/s) as well as % of errors

Compound	D_{exp}	D_{Stine}	D	% of error, Stine data ^a	% of error, this work ^b
ABH	7.60	7.63	7.60	0.3990	0.0007
BTF	8.49	8.50	8.49	0.1415	0.0003
BTNEU	9.01	8.95	9.01	0.6775	0.0004
HMX	9.12	9.02	9.12	1.0090	0.0001
TNETB	8.46	8.48	8.46	0.2300	0.0006
Exp1D	6.85	6.86	6.85	0.1644	0.0000

^a % of error = $100 * |(D_{exp} - D_{Stine}) / D_{exp}|$

^b % of error = $100 * |(D_{exp} - D) / D_{exp}|$

Once each term in equation (6) is determined, it is thereafter possible to calculate the detonation velocities for the explosives selected in this study – PETN, RDX and TATB. Hence, using equation (6), detonation velocities D were calculated for these compounds and are reported in Table 5, along with experimental values D_{exp} . A very good agreement is observed when comparing experimental and calculated values of D . Note that HMX is at the same time a molecule under this study and a molecule used in the Stine model for the calculation of various constants used in equation (6) to compute the detonation velocity. The correlation with experimental data of HMX is therefore obviously perfect, and is not showed in Table 5.

Table 5. Detonation velocities for PETN, RDX, and TATB in km/s

Chemical Formula	Compound	D_{exp} "(Cooper, 1996)"	D
$C_3H_6N_6O_6$	RDX	8.70	8.73
$C_5H_8N_4O_{12}$	PETN	8.26	8.29
$C_6H_6N_6O_6$	TATB	7.76	7.91

3.3 Rayleigh Line and Hugoniot

The Hugoniot curve is defined when the pressure is expressed as a function of the specific volume, $p = f(v)$, in the p - v plane as shown in Figure 3. Furthermore, the Hugoniot curve represents the locations of all equilibrium states for a specific material under pressure. The Rayleigh line is defined as the line joining the initial and final states on the p - v Hugoniot curve, as showed in Figure 3.

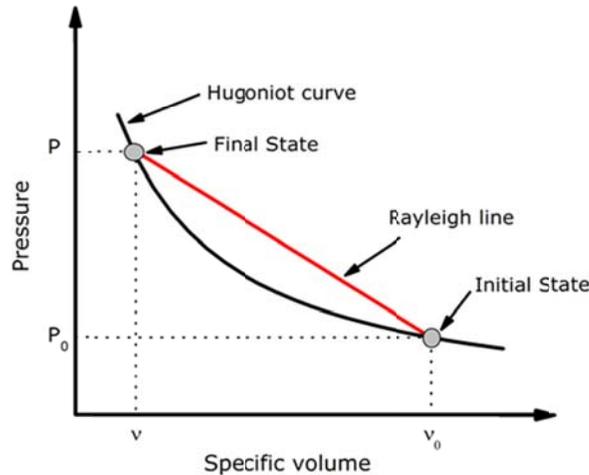


Figure 3. Example of p - v Hugoniot curve and Rayleigh line

The Rayleigh line and Hugoniot curves of the gaseous products were obtained by using the simplest prediction theory of detonation in gases, known as the Chapman-Jouguet (CJ) theory. This theory uses a set of algebraic equations to model the detonation under the assumption that the propagation of the shock wave is accompanied by an exothermic energy release. This theory is discussed in more details in most shock physics textbooks "(Carlucci and Jacobson, 2007;

[Fickett and Davis, 2000](#))".

Using the conservation of mass, momentum and energy equations, the Rayleigh line is a consequence of combining the mass and momentum conservation relations:

$$\rho_0^2 D^2 - \frac{(p - p_0)}{(v_0 - v)} = 0 \quad (7)$$

which is expressed in terms of specific volume $v = 1/\rho$, pressure p and detonation velocity D .

An ideal gas is characterised by a constant heat capacity, when the temperature range is sufficiently small, and a constant heat $q = \Delta H_r^0$ for a complete reaction. The Hugoniot curve is then expressed as a function of v/v_0 , p/p_0 , q , λ and μ according to equation (8):

$$\left(\frac{p}{p_0} + \mu^2 \right) \left(\frac{v}{v_0} - \mu^2 \right) - 1 + \mu^4 - \mu^2 \frac{2\lambda q}{p_0 v_0} = 0 \quad (8)$$

where $\mu^2 = (\gamma - 1)/(\gamma + 1)$, and $\gamma = C_p/C_v$ is the ratio of specific heats. λ is the degree of conversion of the chemical reaction, changing from 0 for no reaction to 1 for a complete reaction. In this work, it is assumed that the reaction is complete, so that $\lambda = 1$. This equation corresponds to a rectangular hyperbola in the $p/p_0 - v/v_0$ plane, centered at the point where $v/v_0 = \mu^2$ and $p/p_0 = -\mu^2$.

If the Hugoniot curve (equation (8)) is solved simultaneously with the Rayleigh line (equation (7)), the intersection of these two equations defines the CJ point at the detonation process. The heat of detonation is represented by q , which can be predicted by quantum mechanical methods "[\(Rice and Hare, 2002\)](#)". In this work, for molecule set considered, heat of detonation q and density ρ_0 values are extracted from the literature "[\(Mader, 2008; Ravi et al., 2011; Yinon and Zitrin, 1993\)](#)" and used in equations (7) and (8) to plot Hugoniot curves of gaseous products and Rayleigh lines. The analytical results for the four explosives, at various corresponding values of

γ , are presented in Figure 4.

Unreacted material passes through the shock wave caused by the detonation process of explosives. As discussed previously, the final state is determined by the intersection of equation (8) and the Raleigh line, equation (7). The accuracy of γ is important because it significantly influences the tangent of the Hugoniot energy, and consequently the CJ point position. As pointed out by Cooper "(Cooper, 1996)", an explicit value of γ is not available, but experiments have shown that it ranges between 2 and 3. Many texts provide approximate values for γ . However, in this work, the aim was also to explore the effect of γ on the Hugoniot curve. For given values of p and v , γ was varied from 2 to 3 for the four explosives.

Table 6. Experimental and calculated ratio of specific heats γ at the p_{CJ} pressure.

	ρ_0 (kg/m ³)	γ		p_{CJ} (GPa)	
		This work	Exp "(Mader, 2008)"	This work	Exp "(Mader, 2008)"
RDX	1800	2.83	2.98	36.45	34.70
HMX	1900	2.89	3.00	40.60	39.30
PETN	1770	2.55	2.64	34.50	33.50
TATB	1895	3.00	2.72	29.23	31.50

Figure 4 shows the effect of γ variations on the Hugoniot curve and its relationship to crossing the Raleigh line. For PETN, when γ is equal to 2.2, the Hugoniot curve intersects the Raleigh line at points A and B. As γ is gradually increased to a value around 2.55, this curve will become tangent to the Raleigh line, and if γ is further increased to 3.0, the Hugoniot curve will lie above the Raleigh line. Similar behaviour is observed for HMX, RDX and TATB. The CJ points were obtained for the four explosives by varying γ , and results are listed in Table 6 and plotted in Figure 4. The γ values compare quite well with the published experimental data.

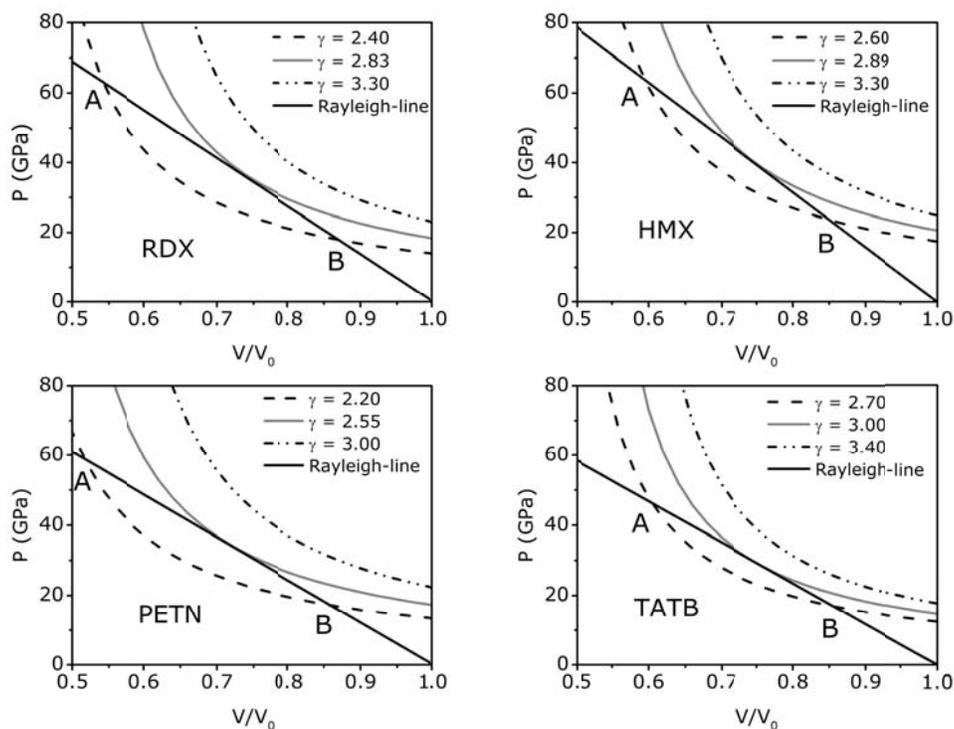


Figure 4. Hugoniot curves demonstrating the effect of changing γ relative to the Raleigh lines

3.3 Unreacted processes of materials

MD simulations were also conducted to determine the Hugoniot properties of RDX, HMX, PETN and TATB molecules, using the Materials Studio (MS) software ("www.accelrys.com"), which includes molecular mechanics (MM) and molecular dynamics (MD) packages. As a starting point, molecular mechanics was used to minimise the energy of crystalline structures. The COMPASS force field was used to describe the molecular interactions, and periodic boundary conditions were imposed ("[Sun, 1998](#)").

As a second step, the NPT (constant number of particles, pressure and temperature) ensemble MD simulations were applied to optimized RDX, HMX, PETN and TATB crystalline structures to compute the p-v Hugoniot curves within a time step of 1 femtosecond (10^{-15} second). These simulations were performed using the Parrinello and Rahman NPT formulation where, in order to simulate the pressure, a mass is assigned to the unit cell. The mass value used for this study

was of 20 atomic mass units "(Parrinello and Rahman, 1981, 1982)". The temperature in all simulations was equilibrated with the Andersen algorithm and fixed at the room temperature for all MD simulations.

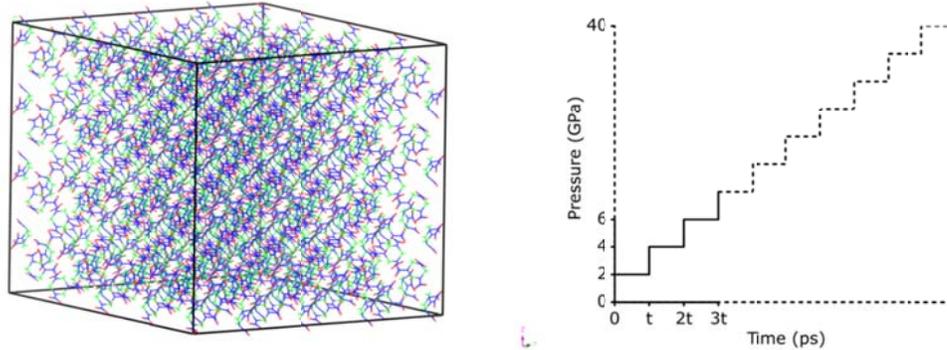


Figure 5. Illustration of the progressive pressure increase during the NPT dynamics simulations

Figure 5 shows NPT dynamics simulations for different pressure values, ranging from 2 to 40 GPa, with a step of 2 GPa. For each pressure, the NPT dynamics simulations were performed within a time-duration, t , of 2 ps (2000 time steps). In order to verify if the simulation time was sufficient for the mass used, the convergence of the p - v curves at various selected time-durations was verified.

An iterative procedure was applied to generate optimized configurations at the end of the simulation. At each fixed pressure, a new density was calculated from changes in the dimension of the supercell, and consequently a new specific density ratio was determined for the material. Table 7 lists relative specific density ratios obtained at various pressures.

One of the problems often encountered when performing molecular dynamics simulations using a force field is that of bond breakage. This is related to the use of a mathematical equation to describe bond energy which, although representative at low energies, fails at higher energies, resulting in bond length increases which are unreasonable and therefore atoms becoming 'disconnected'. During the NPT dynamics simulations, no bond breaking was observed in the

present case, which is attributed to the mathematical formula used of bond-stretching energy calculations in the COMPASS force field, as discussed by Politzer and Boyd "([Politzer and Boyd, 2002](#))".

Table 7. Relative specific density ratio v/v_0 obtained at different MD simulation pressures

	RDX	HMX	PETN	TATB
p^a (GPa)	v/v_0	v/v_0	v/v_0	v/v_0
2	0.89	0.92	0.88	0.94
4	0.82	0.86	0.82	0.89
6	0.78	0.82	0.79	0.85
8	0.76	0.79	0.76	0.82
10	0.73	0.77	0.74	0.79
12	0.72	0.75	0.72	0.78
14	0.70	0.73	0.71	0.76
16	0.69	0.71	0.69	0.75
18	0.67	0.70	0.68	0.74
20	0.66	0.69	0.67	0.72
22	0.65	0.68	0.66	0.71
24	0.64	0.67	0.65	0.71
26	0.64	0.66	0.65	0.70
28	0.63	0.65	0.64	0.69
30	0.62	0.64	0.63	0.68
32	0.61	0.64	0.62	0.67
34	0.61	0.63	0.62	0.67
36	0.60	0.62	0.61	0.66
38	0.60	0.62	0.61	0.66
40	0.59	0.61	0.60	0.65

^a Pressure values of the four different explosives were slightly different. They were rounded to integers in the table.

A comparison between molecular dynamics simulation and experimental results is presented in Figure 6. The experimental Hugoniot diagrams in the condensed phase for RDX, HMX, PETN and TATB "([Olinger et al., 1975](#); [Stevens et al., 2008](#); [Yoo and Cynn, 1999](#))" are in excellent agreement with those obtained from molecular dynamics calculations.

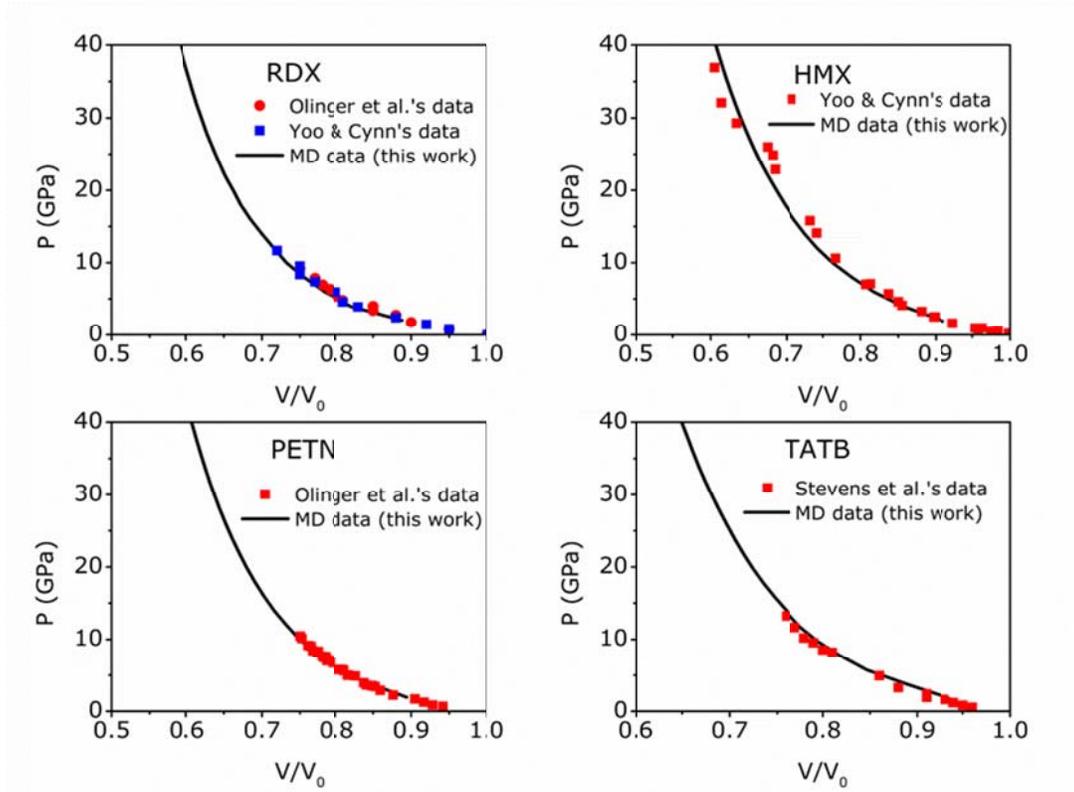


Figure 6. The compression p - v of unreacted explosives obtained using MD simulations as compared to experimental values

3.4 Shock and particle velocity calculations

The shock wave and particle velocities represent the most important parameters needed for shock processing. The shock wave exerted on a material at a constant velocity U_s (shock velocity) causes motion of this material with a particle velocity u_p . Many experiments have been conducted to establish the relationship between U_s and u_p , and it was found that, as a first approximation, U_s shows a linear behavior regarding u_p , for most explosives considered in this work. In this case, U_s would simply follow the linear equation (9) "(Cooper, 1996)":

$$U_s = C_0 + su_p \quad (9)$$

where C_0 is a constant named the bulk sound speed and s is the slope of the U_s - u_p curve. The velocity plot U_s versus u_p can be built from p - v data and the density of material using Rankine – Hugoniot jump conditions proposed by Bart Olinger and Howard Cady at Los Alamos National

Lab, as described by "[\(Peiris and Gump, 2008\)](#)". The jump conditions at the shock are given by the principles of conservation of mass, momentum and energy across the shock, namely,

$$\rho(U_s - u_p) = \rho_0 U_s \quad (10)$$

$$p + \rho(U_s - u_p) = p_0 + \rho_0 U_s \quad (11)$$

$$e_1 + pv + \frac{1}{2}(U_s - u_p)^2 = e_0 + p_0 v_0 + \frac{1}{2}U_s^2 \quad (12)$$

U_s and u_p are consequences of combining the mass and momentum conservation relations for an initial pressure p_0 equal to zero:

$$U_s = \sqrt{\frac{p}{\rho_0(1 - v/v_0)}} \quad (13)$$

$$u_p = \sqrt{p(1 - v/v_0)/\rho_0} \quad (14)$$

Using these two equations, (13) and (14), and the results presented in Table 7, the associated shock speed, U_s , and particle velocity, u_p , for each pressure p , and relative volumetric change v/v_0 , can be calculated. Table 8 shows the shock and particle velocities for the four explosives used in this study.

The unreacted explosives U_s - u_p Hugoniot data are reported in "[\(Cooper, 1996\)](#)" and experimental shock compression data for the compounds used in this study are reported for pressures u_p to 15 GPa, except for HMX, for which Yoo and Cynn "[\(Yoo and Cynn, 1999\)](#)" reported pressure-volume values for pressures up to 45 GPa. For the condensed phase, it is assumed that the effect of temperature is negligible for both experiments and numerical simulations. This is arguably a good assumption given that the material is being compressed very quickly (2 ps) and has not reacted yet. It is still a solid, and the pressure-volume relation of solid compounds depends only

slightly on temperature. During simulations, the number of molecules is constant in the unit cell for all compounds throughout the pressure range considered and the shock-induced heating effects are negligible for all isotherm data. Figure 7 shows the graphs for the U_s - u_p data presented in Table 8 and available experimental data taken from "([Olinger et al., 1975](#); [Stevens et al., 2008](#); [Yoo and Cynn, 1999](#))".

Table 8. Calculated U_s and u_p values for unreacted explosives at different pressures p , in km/s

p^a (Gpa)	RDX		HMX		PETN		TATB	
	U_s	u_p	U_s	u_p	U_s	u_p	U_s	u_p
2	3.17	0.36	3.50	0.27	3.22	0.34	3.67	0.22
4	3.50	0.63	3.73	0.53	3.75	0.59	4.19	0.47
6	3.90	0.84	4.00	0.73	4.11	0.82	4.39	0.67
8	4.26	1.04	4.28	0.91	4.44	1.01	4.69	0.85
10	4.54	1.22	4.56	1.07	4.73	1.19	4.94	1.01
12	4.83	1.37	4.79	1.22	5.01	1.34	5.20	1.17
14	5.08	1.52	5.01	1.36	5.25	1.49	5.46	1.31
16	5.30	1.67	5.22	1.49	5.49	1.63	5.69	1.44
18	5.51	1.80	5.41	1.62	5.71	1.77	5.89	1.56
20	5.72	1.93	5.60	1.74	5.91	1.89	6.09	1.68
22	5.92	2.06	5.78	1.86	6.11	2.02	6.28	1.79
24	6.10	2.17	5.94	1.97	6.30	2.14	6.46	1.90
26	6.28	2.29	6.11	2.07	6.47	2.25	6.63	2.01
28	6.44	2.40	6.26	2.18	6.64	2.36	6.80	2.11
30	6.61	2.51	6.41	2.28	6.81	2.47	6.96	2.21
32	6.77	2.61	6.56	2.38	6.97	2.57	7.10	2.31
34	6.92	2.71	6.69	2.47	7.13	2.67	7.25	2.41
36	7.07	2.81	6.83	2.57	7.27	2.77	7.39	2.50
38	7.22	2.91	6.96	2.66	7.42	2.87	7.53	2.59
40	7.36	3.00	7.09	2.75	7.56	2.96	7.66	2.68

^a Pressure values of the four different explosives were slightly different. They were rounded to integers in the table.

Yoo et al. "([Yoo et al., 1998](#))" reported that, during MD compression simulations of a α -RDX crystal, a phase transition leading to the γ -RDX form is observed around 4.2 GPa, whereas Munday et al. "([Munday et al., 2011](#))" observed this γ -phase at 5.2 GPa. In the present work, no crystal phase conversion has been observed for RDX, as shown by the small variations in the radial distribution function (RDF) reported in Figure 8.

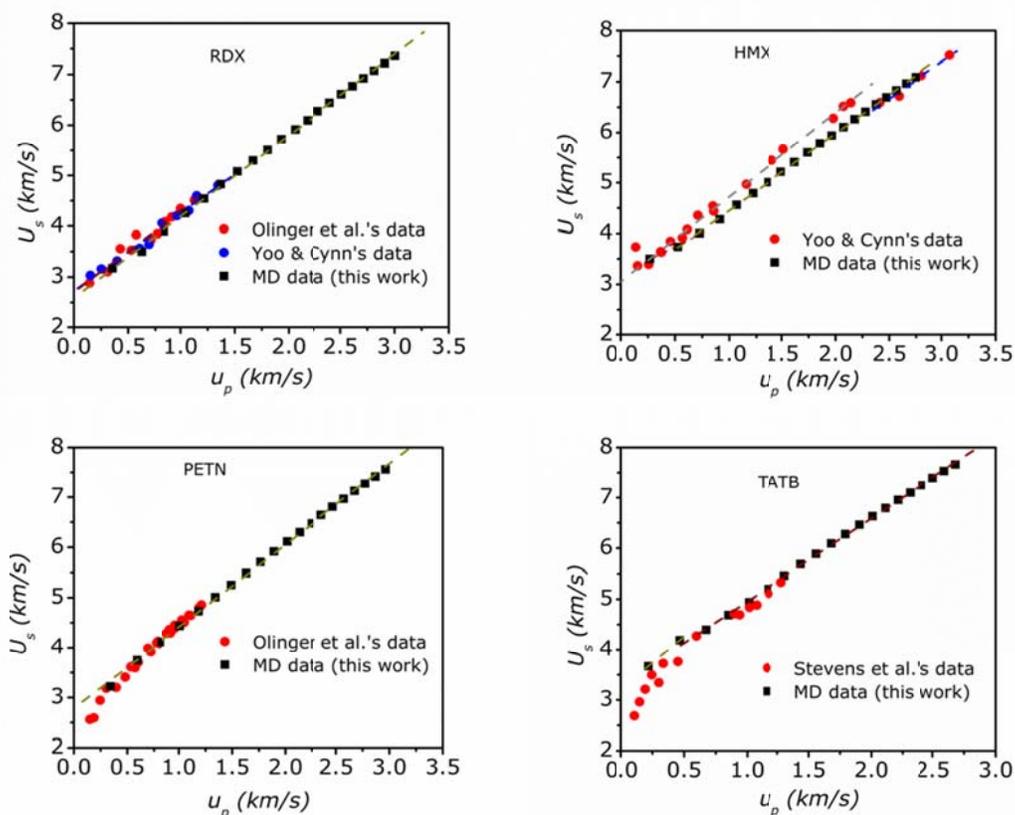


Figure 7. U_s - u_p plot for RDX, HMX, PETN, and TATB compounds as determined from MD in this work and experimental values reported in the literature. The dashed line is the fit of U_s - u_p plot

As shown in Figure 6, in spite of the absence of an observed phase transition, the RDX simulation results compare well with isothermal experimental sets taken from "[\(Peiris and Gump, 2008\)](#)". This is proposed to stem from the relatively limited changes in molecule conformation upon transition from the α to the γ phase. With half of the molecules, one of the three nitro groups changes from the axial orientation in the α form to an intermediate conformation between the axial and the equatorial conformation in the γ form. Further, this transition was shown to occur with retention of crystalline order "[\(Davidson et al., 2008\)](#)".

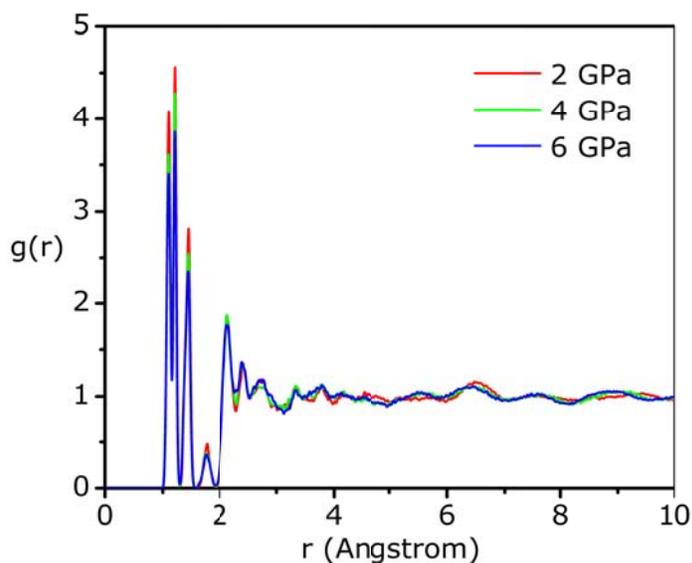


Figure 8. The radial distribution function of α -RDX at $P = 2, 4, 6$ GPa and $T = 298K$

For PETN and TATB, results show a good agreement between the MD compression simulation data and the isotherm p-v values obtained by Olinger et al. and Stevens et al., respectively "(Olinger et al., 1975; Peiris and Gump, 2008; Stevens et al., 2008)". In general, for compressed compounds such as HMX, PETN, RDX and TATB, the U_s-u_p relation is described in terms of a linear equation given by equation (9). However, Figure 7 shows that, for some compounds, the shock velocity variation is not strictly linear with particle velocity for the entire data range but only for segments of the data. The material response is categorized by straight-line segments showing the transition change regions which could be caused by phase or size changes in the crystal lattice "(Cooper, 1996)". The HMX molecule has more conformational degrees of freedom than RDX, and at least four polymorphs exist, having different conformations and crystalline systems (monoclinic for the most stable β form to orthorhombic for the α form and hexagonal for the δ form)"(Liu et al., 2012)". The β to δ transition has been pointed out as the main cause for the increased sensibility of HMX when heated "(Asay et al., 2003)". This may

explain why this specific compound shows more deviation from linearity.

Using a linear regression method for calculated and experimental isothermal data in Figure 7, the C_0 and s parameters were estimated using the OriginPro 9 Software ("www.originlab.com").

In this regression approach, the lower confidence interval (LCI) and upper confidence interval (UCI) of the fit constants are 95% confidence level.

Tables 9 and 10 provide detailed summaries of the linear fit results for experimental isothermal and predicted data, respectively.

Table 9. U_s - u_p Hugoniot data for HMX, PETN, RDX and TATB using experimental isothermal data.

	C_0	s	Range limitations u_p (km/s)	Ref.
HMX	3.05	1.66	0.24-2.14	" (Yoo and Cynn, 1999) "
	3.03	1.45	> 2.4	
PETN	2.76	1.70		" (Olinger et al., 1975) "
RDX	2.73	1.53		" (Yoo and Cynn, 1999) " and " (Peiris and Gump, 2008) "
TATB	2.92	2.09	$0.3 < u_p < 0.9$	" (Stevens et al., 2008) "
	3.33	1.53	> 0.9	

In the case of HMX, the predicted values at high and low u_p values are in good agreement with those reported by Yoo and Cynn "[\(Yoo and Cynn, 1999\)](#)". For PETN, the gap between measured and predicted results remains very small. The linear regression for the predicted data of RDX is in good agreement with experimental measurements. For the TATB molecule, which is the most insensitive explosive studied, the predicted U_s - u_p Hugoniot curves are in good agreement too with data from Stevens et al "[\(Stevens et al., 2008\)](#)".

Table 10. Predicted U_s - u_p Hugoniot data for HMX, PETN, RDX and TATB using MD

	C_0	LCI	UCI	s	LCI	UCI	Range limitations u_p (km/s)
HMX	3.19	2.03	4.03	1.08	-0.46	2.64	0.27-0.73
	2.94	2.89	2.96	1.52	1.51	1.54	> 0.91
PETN	2.78	2.73	2.84	1.63	1.60	1.66	
RDX	2.59	2.54	2.64	1.60	1.58	1.63	
TATB	3.22			2.08			< 0.50
	3.31	3.26	3.35	1.64	1.62	1.66	> 0.64

4. Conclusions

Using quantum mechanics calculations coupled with analytical methods for four energetic materials named RDX, HMX, PETN and TATB, it is possible to estimate some parameters that define the detonation of CHNO based explosives, more specifically the detonation velocity, the Chapman-Jouguet pressure and the density. Detonation velocities of explosives were obtained using Stine's equation. Newer and seemingly more accurate constants were previously obtained for this equation, using an accurate and more optimized algorithm for the least squares fitting "[\(Jaidann et al., 2013\)](#)". With these new constants, a better fit was found with experimental values.

The Rankine – Hugoniot equations were used to calculate the shock and particle velocities. Using these velocities, the pressure to specific density Hugoniot diagrams were constructed. The specific heat ratio, a parameter found in the energy Hugoniot equation for the products, and the Chapman-Jouget pressures and specific densities were obtained for the four explosives using the point where the Raleigh line is tangential to this Hugoniot. Values obtained for the Chapman-

Jouget parameters and specific heat ratios compare well with published experimental values for all four explosives. A sensitivity analysis of the specific heat ratio was executed and it was shown that the tangent the energy Hugoniot makes with the Raleigh line is quite sensitive to exact value of γ , and that care needs to be taken in its determination since the Chapman-Jouguet parameters are determined using this tangential point.

The present work, using a molecular modelling approach together with analytical methods, shows that CHNO based explosives can be numerically characterised and parameters such as CJ, specific heat ratio, γ , p_{CJ} and detonation velocities can be obtained quite accurately prior to experiments. This approach can be used as supporting information to minimise the number of experiments needed.

The potential use of molecular dynamics simulations in predicting shock response of explosives in condensed phase under extreme pressures was studied. Transformation of p-v data to U_s-u_p Hugoniot curves offers the possibility to estimate at least qualitatively the bulk sound speed, for four compounds at high pressures. In the case of HMX and TATB, analysis of simulation data reveals two regions corresponding to U_s-u_p Hugoniot values. The predicted C_0 , bulk sound speed, and s , slope of the U_s-u_p curve, values for RDX, HMX, PETN and TATB are in good agreement with those reported in literature. Molecular dynamics simulations are useful for a better monitoring and understanding of the shocked materials responses, at an atomistic level point a view. From the predicted U_s-u_p Hugoniot curves for unreacted explosives, it is now possible to contemplate further studies involving liquids, homemade explosives and unknown materials. This method can be of assistance to provide appropriate vehicle or/and personnel protections needed by personnel working with explosive materials.

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