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On the explicit determination of the Chapman-Jouguet parameters for an explosive compound

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Abstract

This work re-examines earlier development and current advances of the shock Hugoniots in anticipation of developing an explicit solution to determine the Chapman-Jouguet (*C-J*) parameters for an explosive compound. A new and simple equation for the *C-J* specific density was obtained as a function of three measureable parameters: initial density, detonation velocity and the heat of detonation. For the ratio of specific heats, γ, an explicit expression as a function of the *C-J* parameters was obtained. The relations were tested for the very well characterise explosives PETN, HMX, RDX, TATB, TNT and the calculated values obtained for the *C-J* parameters and γ, compared very well with published experimental values. The equations were then applied to a broad range of explosives types regardless of their heterogeneity or their physical state and the *C-J* parameters obtained compared very well with published values.

Keywords: Chapman-Jouguet parameters, *C-J* parameters, detonation velocity, energetic materials characterisation, explosive characterisation

1. Introduction

The text by Akhavan [1] explains with ample detail the basic principles needed to understand the detonation mechanisms of explosions by chemical explosives especially from a thermochemistry standpoint. The history, theory and chemical types of explosives are introduced and thus provide the reader with information on important physical parameters of primary and secondary explosives. At this time there are still significant constraints in studying the processes of energetic materials especially when it concerns the understanding of associated phenomena such as initiation and detonation at least from an analytic/numerical standpoint. Nonetheless, significant progress has been made within the last two decades. On the subject of explosive compounds many texts such as Akhavan [1] and reviews such as that done by Sorescu, Rice and Thompson [2] have shown that extensive experimental and theoretical attempts have been made to unravel the mix of various fundamental chemical and physical processes that occur during the conversion of the quiescent energetic material to its final products, with the anticipation that the relative importance and contributions of each step in the overall process can be identified and understood. Further, as pointed out by Sorescu, Rice and Thompson [2], from a chemistry standpoint, the revelation of these fundamental processes are next to impossible through experimental observations and measurements alone. Experimental studies of the chemical reactions involved, including studies at the micro and nano scales, have shown that it is difficult to extract meaningful results mainly because of the extreme intensity of the detonation waves and by the scales of these phenomena in time, which is typically of the order of nanoseconds, and length, which is of the order of 10 to 100 Å. As a result, models with varying degrees of sophistication have been developed in an effort to interpret and extrapolate these experimental measurements that are made in the investigation of the conversion of the initial unshocked energetic material to its final products. In recent years, many newer methods both analytic and numerical, such as molecular dynamics, have provided fresh approaches to examining the fundamental processes that are involved in the release of the energy from energetic compounds. These processes include condensed phase reactions, diffusion and transport phenomena, interactions and reactions of transient intermediates in the condensed phase, evaporation of species into the gas phase and reactions of the flame. All these processes occur at extremely small time and space scales as described above. A study by Jaidann et al. [3] on the potential use of molecular dynamics have shown that it is now possible to determine important characteristic properties such as the detonation velocity and the Chapman-Jouguet (*C-J*) pressure and density of energetic compounds quite accurately, at least for the Carbon, Hydrogen, Nitrogen and Oxygen (*CHNO*) based explosives. What this study appears to reveal is that the issue of energetic materials is studied from two principal scientific communities the thermochemistry group and the shock physics community and if one were to try to pull together the advances of each of these communities it might very well be possible to obtain the *C-J* parameters explicitly.

2. Objective

To characterise an energetic material, a series of experiments ranging from slow cook off of the material to high velocity flyer plate impact tests are necessary to obtain parameters such as the detonation velocity, shock and particle velocities and critical pressures that are necessary to obtain the *C-J* parameters. These define the pressure and density necessary for steady state detonation to occur. Although there are many approximate solutions, an explicit solution for the *C-J* parameters as a function of relatively easily measureable parameters is quite difficult mainly because as described in many texts on the subject such as Taylor [4], Fickett and Davis [5], Kuo [6], Cooper [7] and more recently Jaidann [3], the ratio of specific heats for the gaseous products has to be estimated. The basic objective of this study is to revisit earlier development and current advances in both the thermochemistry and the shock physics domain to examine the possibility of arriving at some precise analytic method that includes easily measurable parameters to characterise an explosive compound. As a first approach, four known and well experimentally characterised *CHNO*-based energetic materials are used to guide the study. These four materials are Cyclotrimethylenetrinitramine (RDX), Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), Pentaerythritol tetranitrate (PETN) and Triamino-trinitrobenzene (TATB).

3. Shock Hugoniots and the Rankine-Hugoniot Jump Conditions

Obtaining the shock Hugoniots and the *C-J* parameters are important characterization parameters of explosive materials and these are usually obtained using basic shock physics and mechanics notions. Shock physics, the study of high intensity highly transient events and how these events affect material behavior, allows one to see if a shock is sufficient to begin and support a chemical reaction such as the detonation process in a reactive compound, for example. The Rankine-Hugoniot jump equations describe how materials react to shock loading and in the case of reacting materials can provide crucial information of the detonation process and whether or not the detonation process can be sustained. A more well-described treatment of the Rankine-Hugoniot jump equations is found in the texts Detonation of Condensed Explosives by Taylor [4], Detonation by Fickett and Davis [5], Combustion Dynamics by Kuo [6] and Explosive Engineering by Cooper [7], to name a few. Other texts such as Ballistics- Theory and Design of Guns and Ammunition by Carlucci and Jacobson [8] also treat the Rankine-Hugoniot jump equations but mostly from an application perspective.

Simply stated a Hugoniot is a curve that contains all possible equilibrium states at which a material can exist when shock loaded at different pressures. It is in fact an empirical derived curve that relates any two of the following variables to each other. The pressure, P, the shock velocity U_s, the particle velocity, u_p, and ν, the specific density. The Hugoniot is not an equation of state although it could be used in a similar manner and is sometimes used as an isentrope even though strictly speaking it is not because entropy does increase across the shock front. The Hugoniot is derived experimentally and as such this makes it very attractive since it can be obtained using numerical simulation such as molecular dynamic simulations. In a very simple case, the velocity Hugoniot is an empirical relationship that relates the velocity of the shock front with the particle velocity and experiments have shown that for most reacting and non-reacting materials it is a simple linear relationship that is expressed in the form

$$U_s = C_0 + s u_p \tag{1}$$

where U_s is the speed of propagation of the shock front, u_p is the particle velocity, C_0 is sometimes called the bulk sound speed but is also the intercept on the U_s axis and s is the particle velocity coefficient obtained experimentally. Figure 1 shows the U_s-u_p curve for PETN for C_0 = 2.6 and s = 1.6. The experimental values for C_0 and s are taken from Cooper [4].

The real power of Equation (2) comes when it is used in conjunction with the equations of conservation of mass, momentum and energy. The three conservation equations taken from Cooper [7] are given below. For a more rigorous treatment of the development of these equations the reader is referred to the text by Taylor [4] or those by Fickett and Davis [5] and Kuo [6].

Conservation of mass:

$$\frac{\rho_1}{\rho_0} = \frac{v_0}{v_1} = \frac{U_s - u_0}{U_s - u_1} \tag{2}$$

Conservation of momentum: $P_1 - P_0 = \rho_0(P_1u_1 - P_0u_0)(U_s - u_0)$ (3)

Conservation of energy: $e_1 - e_0 = \frac{(P_1u_1 - P_0u_0)}{\rho_0(U_s - u_0)} - \frac{1}{2}(u_1^2 - u_0^2)$ (4)

where the subscript '0' is for conditions ahead of the shock front and '1' is for after the shock wave has passed. Equations (1) to (4) can be applied to all materials under shock loading conditions.

Now if Equation (1) is combined with the continuity equation (2) and the momentum equation (4) and setting $\nu = \frac{1}{\rho}$ which is the specific density, a Hugoniot of the form given by Equation (5) below is obtained

$$P_1 = \frac{C_0^2(\nu_0 - \nu_1)}{[\nu_0 - s(\nu_0 - \nu_1)]^2} \tag{5}$$

Equation (5) is an extremely powerful relationship because it is the Hugoniot that provides the pressure, *P*, as a function of the specific density, *v*. So for any change in density the final pressure jump on the solid Hugoniot can be obtained. This pressure jump occurs in the form of a shock wave along what is called the *Rayleigh line*. The equation for the *Rayleigh line* is derived very easily by combining the mass and momentum equations and setting for convenience the initial particle velocity $u_0 = 0$ to get

$$P_1 - P_0 = \frac{U_s^2}{\upsilon_0} - \frac{U_s^2}{\upsilon_0^2}\upsilon_1 \tag{6}$$

Figure 2 shows the solid Hugoniot and the *Rayleigh line* on the P - ν diagram. Interpreting the Hugoniot and the *Rayleigh line* in terms of shocking a material, a jump will take place through the forming of a shock wave and will proceed along the *Rayleigh line,* XAC, to another equilibrium level, A, on the Hugoniot for the solid material.

3.1 Shock Hugoniot for explosive characterisation

Equations (1) to (4) can be used for all materials under shock loading conditions. However, in the case of explosives there are some differences in the Hugoniot curves. In fact, once the chemical reaction has taken place a different material is formed and a shock wave present in this material will have a different Hugoniot. The continuity equation (2) can be rewritten as a function of the detonation velocity, *D,* to get

$$\rho_0 D = \rho_1 (D - u_p) \tag{7}$$

In fact, the shock propagation velocity, U_s, in the continuity equation is replaced by *D,* the detonation velocity, and setting for simplicity $u_0 = 0$. Similarly, the conservation of momentum equation (3) could be rewritten as

$$P_1 - P_0 = \rho_0 D u_p \tag{8}$$

Eliminating u_p using Equations (7) and (8), the *Rayleigh line* is obtained in the form of

$$\rho_0^2 D^2 - \left(\frac{P_1 - P_0}{\nu_0 - \nu_1}\right) = 0 \tag{9}$$

Rearranging the terms in Equation (9), the *Rayleigh line* could be rewritten as

$$P_1 = (P_0 + \rho_0^2 D^2 \nu_0) - \rho_0^2 D^2 \nu_1 \tag{10}$$

From Equation (10) it is readily seen that the slope of the *Rayleigh line* is $-\rho_0^2 D^2$. Now if D is eliminated using Equations (7) and (8), with some algebraic manipulation the following Hugoniot curve for the particle velocity, u_p, is obtained.

$$u_p^2 = (P_1 - P_0)(\nu_0 - \nu_1) \tag{11}$$

Hence, if the detonation velocity D and the particle velocity u_p are known, basically all is known for the solid material because the intersection of the Hugoniot curve and the Rayleigh line can be found.

The next step is the development of the Hugoniot for the products which follow the detonation of the solid explosive. Consider rewriting the energy equation as

$$e_1 - e_0 - \frac{1}{2}(P_1 + P_0)(\nu_0 - \nu_1) = 0 \tag{12}$$

Equation (12) is the energy difference between the two states of the explosive, the '0' and the ‘1’ states described earlier.

At this stage it would be worthwhile to go through the basic development of the products Hugoniot for clarity and completeness. In its simplest form it is assumed for Equation (12) that the '0' state represents the fact that the reaction has not yet begun whereas for the '1' state the reaction has been completed. For a polytropic gas

$$pv\ = RT \tag{13}$$

where p is the pressure and v is the specific density. T is the temperature and R is the gas constant. The energy equation can be written as

$$e = \ C_v T - \ \lambda q \tag{14}$$

where e is the energy, C_v is the specific heat at constant volume,. $q = \ \Delta h_r^0$ is the heat released from the reaction, and. Δh_r^0 is the heat of reaction of the complete reaction. $\lambda = 0$ simply means the reaction has not yet begun whereas $\lambda = 1$ means the reaction is complete. It is known that $R = \ C_v(\gamma - 1)$ so rewriting Equation (13) and substituting for R, the following equation for T can be obtained

$$T = \frac{pv}{C_v(\gamma - 1\ )} \tag{15}$$

Substituting for T in Equation (14) the energy can now be written as

$$e = \ \frac{pv}{(\gamma - 1)} - \ \lambda q \tag{16}$$

Using Equation (16) in Equation (12) the equation for the Hugoniot of the products can now be given on the $p - v$ Hugoniot diagram and could be written with some algebraic manipulation as

$$\frac{P_1 v_1}{\gamma - 1} - \frac{P_0 v_0}{\gamma - 1} - \ \lambda q - \frac{1}{2}(P_1 + P_0)(v_0 - \ v_1) = 0 \tag{17}$$

Defining $\mu^2 = \frac{(\gamma-1)}{(\gamma+1)}$ then Equation (17) can be rewritten as

$$\left(\frac{P_1}{P_0} + \mu^2\right)\left(\frac{\nu_1}{\nu_0} - \mu^2\right) - 1 + \mu^2 - \mu^2 \frac{2\lambda q}{P_0 \nu_0} = 0 \qquad (18)$$

Equation (18) is a hyperbola in the $\left(\frac{\nu}{\nu_0}, \frac{P}{P_0}\right)$ plane and is centered at $\frac{\nu}{\nu_0} = \mu^2$ and $\frac{P}{P_0} = -\mu^2$

Equation (18) is the Hugoniot that defines all possible end states of the detonation process and if solved simultaneously with the *Rayleigh line* their intersection will define the state of the gas emerging from the detonation reaction. Figure 3 below shows a typical Hugoniot, *XIABE*, for the solid material given by Equation (5). A typical Hugoniot for the products is given by Equation (17) is shown by curve *HDCF*. With regards to the *Rayleigh line* there are three possible solutions when defining the interaction of Equation (10) with Equation (18). Firstly, if the detonation velocity is such that the Rayleigh jump condition is along *XIJ* which is below the products Hugoniot, *HDCF*, then this simply means that the jump does not involve the products and the explosive simply did not detonate because the products are formed only when detonation has occurred. In the case where the *Rayleigh line* crosses the products Hugoniot at two points *C* and *D* would imply that at point *C* the rarefaction wave velocity would be greater than the detonation velocity and would be overtaking the shock front which is not possible. At the lower point *D* the rarefaction wave velocity would be much lower than the velocity of the shock front making the reaction zone spread out continuously in time which again is not possible if detonation is to be sustained. The only place on the products Hugoniot where the slope of the Hugoniot equals the slope of the *Rayleigh line*, the reaction zone, the rarefaction front and the shock front are all at the same velocity is at the tangent point which is the *C-J* state shown as the

C-J point in Figure 3. A more rigorous discussion of these solutions can be had from, Taylor [4], Fickett and Davis [5], Kuo [6], Cooper [7] or Carlucci and Jacobson [8].

3.2 The influence of ratio of specific heats, γ, on the energy Hugoniot

In its simplest form in the detonation process of an explosive the reaction occurs immediately and this implies that once the unreacted material passes through the detonation wave, it is instantaneously converted to a new material and as discussed previously the final state is determined by the intersection of Equation (18) and the *Rayleigh line* given by Equation (10). The correct value of γ which is the ratio of the specific heat at constant pressure to that at constant volume, C_p/C_v , is important because it influences significantly the tangent that the energy Hugoniot makes with the *Rayleigh line* and as a result will influence the *C-J* point. As pointed out by Kuo [6], Cooper [7] and many references on the subject, an explicit value of γ is not available but experiments have shown that it ranges between 2 and 3. Many texts and studies provide approximate or iterative methods for obtaining γ. A recent study by Jaidann et al. [3] explored the influence of γ on Equation (17). For values of P and v_1/v_0, γ was varied between 2 and 3 for the four explosives and it was found that for very small changes in γ the tangent point formed by the energy Hugoniot, Equation (18), and the *Rayleigh line* could vary significantly. Figure 4 below shows the effect of γ on the energy equation with P as a function of the relative specific density, v_1/v_0, which in this case is for PETN. For γ equals 2.2, Equation (17) intersects the *Rayleigh line* at two points and as γ is gradually increased at some point it is tangent to the *Rayleigh line* and if further increased it stays above the *Rayleigh line*. The value of $\gamma = 2.65$ compares very well with the published experimental value of 2.6 but more notably, the results described highlight the significance and influence of γ on the determination of the *C-J* parameters. Thus, arriving at an explicit solution for γ could prove to be extremely useful and this is treated in the following section.

4. The Taylor equations

In the previous section the Chapman-Jouguet pressure and relative specific density, P_{CJ} and ν_{CJ}, respectively, were found by choosing an initial value for γ somewhere between 2 and 3 then plotting the energy Hugoniot on the *p*-*v* plane as shown in Figure 4. γ was then adjusted until the energy Hugoniot was tangent with the Rayleigh Line. The point of tangency defines the *C*-*J* point and, hence, P_{CJ} and ν_{CJ}.

In 1952 Taylor in his text Detonation in Condensed Explosives [4] rigorously examined the hydrodynamic theory of detonation. Using the definitions of the *C*-*J* conditions, the conditions for thermodynamic equilibrium, the three conservation equations and the energy equation for the explosive products he derived some very important and significant relations with regards to approximate properties of stable detonation in an explosive. The author refers the reader to Taylor's text [4] especially Chapter XI and would not attempt to redevelop the relations stated below. The essential relations are as follows:

$$v_{CJ} \cong \frac{\gamma v_0}{\gamma + 1} \tag{19}$$

$$P_{CJ} \cong \frac{2q(\gamma - 1)}{v_0} \tag{20}$$

$$T_{CJ} \cong \frac{2q\gamma}{(\gamma + 1)c} \tag{21}$$

$$W_{CJ} \cong \sqrt{\left\{2q\frac{\gamma-1}{\gamma+1}\right\}} \tag{22}$$

$$D \cong \sqrt{\{2q\gamma^2-1\}} \tag{23}$$

where v_{CJ}, P_{CJ}, T_{CJ}, are the *C-J* density, pressure and temperature, respectively. W_{CJ} is the particle velocity or what is sometimes called the stream velocity, D is the detonation velocity while q and γ are, respectively, the heat of explosion and the ratio of specific heats. What is particularly striking in Equations (19) to (23) is the presence of γ and yet even though these equations have been used extensively in various forms γ still has to be guessed at or obtained experimentally.

Additionally to Equations (19) to (23), Taylor [4] reasoned and showed quite easily from the above equations that if P_1 and T_1 are the pressure and temperature reached in an explosion at constant volume, then

$$\frac{T_1}{T_{CJ}} = \frac{2\gamma}{\gamma+1} \tag{24}$$

$$\frac{P_1}{P_{CJ}} = 2 \tag{25}$$

Taylor [4] further explained that these last two equations are not restricted to ideal gases but in fact remain approximately true for all explosives. This is an important fact but Taylor [4] stopped at this point on the clear use of these last two equations and as far as the author has read in the literature no further explicit reference or use has been made with these equations. However, it seems that these two equations have significance importance given that they are valid at constant volume and are not restricted to ideal gases. These equations are used in the following discussion below towards an explicit determination of the *C-J* parameters.

4.1 An explicit determination of the *C-J* parameters and γ as a function of three measurable parameters

Let's consider restating the energy equation (12) for the explosive products with the particle initial velocity $u_0 = 0$

$$e_1 - e_0 - \frac{1}{2}(P_1 + P_0)(v_0 - v_1) = 0 \tag{26}$$

Putting $\Delta E = e_1 - e_0$, replacing P_1 with $2P_{CJ}$ using Taylor's equation (25) above and rearranging the terms algebraically the following equation for P_{CJ}, the *C-J* pressure, can be obtained

$$P_{CJ} = \frac{\Delta E}{v_0 - v_{CJ}} - \frac{P_0}{2} \tag{27}$$

The argument here to replace P_1 with $2P_{CJ}$ is in fact that P_1 is the maximum pressure reached in the solid explosive at constant volume as the temperature rises and the initiation of the chemical reaction occurs thereby initiating the energy release. P_1 is actually found on the solid Hugoniot but most times P_1 is treated as the Rayleigh jump pressure or the von Neumann pressure on the solid Hugoniot. This work treats P_1 as a pressure on the solid Hugoniot which is higher than the von Neumann pressure and is equal to $2P_{CJ}$. The implication of this interpretation of the Taylor equation suggests that there exists a pressure higher than the von Neumann pressure on the solid Hugoniot at which the initiation of the chemical reaction is initiated and it is $2P_{CJ.}$ .This implication is currently being investigated further by the author

With regards to Equation (27), ΔE represents the total energy change that would occur as the explosive pass from (P_1, T_1) to (P_{CJ}, T_{CJ}) into the actual *C-J* products and is in fact sometimes called the heat of detonation. Now differentiating P_{CJ} with respect to v_{CJ} the following relation is obtained

$$\frac{dP_{CJ}}{dv_{CJ}} = \frac{\Delta E}{\left(v_0 - v_{CJ}\right)^2} \tag{28}$$

It has been established that the *C-J* point is defined by the tangent that the *Rayleigh line* makes with the energy equation given by Equation (27). This implies that $\frac{dP_{CJ}}{dv_{CJ}}$ must equal the slope of the *Rayleigh line* given earlier by Equation (10) as $-\frac{D^2}{v_0^2}$ where $v_0^2 = \frac{1}{\rho_0^2}$. Therefore, replacing $\frac{dP_{CJ}}{dv_{CJ}}$ by $-\frac{D^2}{v_0^2}$ in Equation (28), Equation (29) below is obtained

$$-\frac{D^2}{v_0^2} = \frac{\Delta E}{\left(v_0 - v_{CJ}\right)^2} \tag{29}$$

Reducing and rearranging Equation (29) with $\frac{v_{CJ}}{v_0}$ as the subject of the equation the following quadratic Equation (30) is obtained

$$\left(\frac{v_{CJ}}{v_0}\right)^2 - 2\frac{v_{CJ}}{v_0} + \left(\frac{\Delta E}{D^2} + 1\right) = 0 \tag{30}$$

Equation (30) could be solved for $\frac{v_{CJ}}{v_0}$ and the two reduced solutions are given below by Equation (31)

$$\frac{v_{CJ}}{v_0} = 1 \pm \sqrt{\frac{\Delta E}{D^2}} \tag{31}$$

Given that $\frac{v_{CJ}}{v_0}$ cannot be greater than 1 only the minus solution is considered. Particularly striking is that even though Equation (31) appears to be simple it is of significant value for two reasons. Firstly, it provides an explicit solution for v_{CJ} that has not been seen in literature that the author has reviewed and secondly, and more importantly, it is a function of three parameters that are very well understood and measureable either experimentally as was done by Dobratz and Crawford [9] or calculated using thermochemical methods as described for example by Akhavan [1] for the heat of detonation, ΔE, and Stein [10] and Keshavarz [11] for the detonation velocity, D. In fact, Keshavrez [11] used the Stein [10] method to obtain detonation velocities for many explosive compounds but he used the gas phase heat of formation $\Delta_f H^0_{gas}$ instead of that for the solid phase. He showed that using the gas phase heat of formation very accurate detonation velocities for a vast number of *CHNO* based compounds at any loading density could be predicted and does not require knowledge of solid or liquid heat of formation which is a parameter not necessarily known or available for many new explosives. This is an interesting development since the gas phase heat of formation is calculated using the basic additive rules.

Returning to Equation (31), it should be noted that the energy term under the square root is negative but since the energy released is exothermic the minus signs will be cancelled for numerical values for the heat of detonation, thus the negative sign is dropped for convenience. Now that v_{CJ} is known implies that P_{CJ} could now be calculated from Equation (27).

At this point one other important parameter remains to be calculated and this is the specific heat capacity ratio, γ. Consider rewriting Equation (17) setting $\lambda = 1$ for a complete reaction, $\Delta E = q$ and with γ as a function of P_{CJ} and v_{CJ} to get the following equation

$$\gamma = 1 + \frac{P_{CJ}v_{CJ} - P_0 v_0}{\Delta E + \frac{1}{2}\left(P_{CJ} + P_0\right)\left(v_0 - v_{CJ}\right)} \tag{32}$$

Given that P_{CJ} and v_{CJ} are now known γ can be obtained explicitly

4.2 Application of the equations to determine the Chapman-Jouguet parameters of PETN, HMX, RDX and TATB

Table 1 below provides a summary of the relations in order of requirement to obtain the *C-J* parameters. The detonation velocity and loading densities are taken from Akhavan [1], Cooper [7] and Dobratz and Crawford [9]. The heat of detonation is taken from Akhavan [1]. These values are shown in Table 2. Table 2 also provides the initial values for PETN, HMX, RDX and TATB required for the equations.

Using the equations given in Table 1 and the relevant parameters provided in Table 2 the *C-J* parameters and γ are obtained for PETN, HMX, RDX and TATB. As shown in Table 3 the calculated values compare quite well with experimental and other published data. It is quite interesting that γ also compares quite well with published experimental data and it was obtained explicitly as a function of the *C-J* parameters. Figure 5 provides a graphical representation of the *Rayleigh line* and the products Hugoniot obtained using the calculated value of γ and so far it appears to conform to publish Hugoniots for these explosive compounds.

5. Application of the equations to a range of explosive types

An attempt is made here to further demonstrate the practicality, usefulness and precision with which the equations developed could be used to determine the *C-J* parameters for other explosive compounds that are well known but are special in many ways. The examples chosen for demonstration are named in Table 4 and are selected based on trying to apply the equations to a broad range of explosive types and at the same time the capability of finding valid experimental data such as the heat of detonation, density, detonation velocity and the associated experimental or accepted *C-J* pressure for comparison. Table 4 also shows the data required for calculating the *C-J* parameters and γ. Table 5 shows the calculated values of the *C-J* pressure, density and γ. The results shown indicate that the equations worked quite well in calculating the *C-J* parameters and γ when compared to the accepted published values.

5.1 A discussion on the calculated C-J parameters

In reviewing the literature, of the three parameters required namely the loading density, the detonation velocity and the heat of detonation, it was found that the heat of detonation was the most difficult to interpret or discern from other definitions of energies such as the heat of explosion and the heat of combustion. Akhavan [1] was one of the few publications that clearly distinguish the differences and expresses the heat of detonation in *J/mol* as the heat generated as the condensed material goes through the detonation process which is defined as from initiation to complete detonation. If all the compounds that make up the explosive material participate in the detonation process then the heat of explosion is the same as the heat of detonation expressed in *J/kg*. Where it becomes not so clear is when an additive such as fuel oil or a metal is used and combusts and burns after the detonation process to produce heat so as to maintain high temperatures and pressures for a longer period of time. In this case, the heat of explosion is different and basically includes the heat of detonation in addition to the heat produced from the combustion and burning of the additive. This definition is significant for the use of the equations developed since only the heat of detonation is required to calculate the *C-J* parameters and as such the definition provided by Akhavan [1] is followed.

There were basically four categories of explosive compounds for which attempts were made to calculate the *C-J* parameters. The first category consists of solid explosives homogenous or heterogeneous for which the heat of detonation in *J/kg* is considered the same as the heat of explosion. These compounds include BTF, LX 04, LX 10, COMP B, TNT, AMATOL, ADN, CYCLOTOL 75/25 and PBX 9502 which is considered to be a heterogeneous explosive compound. For these materials there were some differences found in the values of the heat of detonation but in general there seems to be consensus on its magnitude within 10 percent whether or not it was called the heat of explosion. The importance here is the general acceptance that all the compounds that make up the explosive material participate in the detonation process regardless of heterogeneity. The calculated *C-J* parameters for all these explosive compounds compare in general well within 6 percent of the published experimental or accepted values.

The second kind of compounds that the equations were applied to was the liquid explosive type. There were basically two compounds considered for this category - nitroglycerine (NG) and nitro-methane (NM) where again the heat of detonation is taken as the heat of explosion. Literature [1], [7], [11], [18] seems to have a consensus on the magnitude of the heat of detonation 6200 *kJ/kg* for NG and 4450 *kJ/kg* for NM. However, it was found that the *C-J* pressure considered as the experimental value varied between 18 to 27 *GPa* for NG and 12 to 14 *GPa* for NM. For the calculation of the *C-J* parameters using the proposed equations, a consistent set of data consisting of the heat of detonation, the detonation velocity and the loading density was formulated from Akhavan [1], Cooper [7], and Dobratz and Crawford [11]. The calculated *C-J* pressures obtained for NG and NM were 30 *GPa* and 14.9 *GPa*, respectively. For NM the calculated value compares quite well with the experimental value whereas for NG a 10 percent difference which corresponds to a 3 *GPa* difference from the accepted experimental value was obtained.

The third category to which the equations were applied was the energised explosive type. These are explosives for which the heat of detonation is not considered the same as the heat of explosion. For the energised explosive additional heat is generated after the detonation by adding to the explosive compound another fuel with a high heat of combustion. Ammonium nitrate with fuel oil (ANFO) and aluminised explosive compositions are examples of these types of explosives. In this study ANFO, HBX-3 and TNT/ALEX-20 are the explosive compounds chosen to calculate the *C-J* parameters. The ANFO heat of detonation was taken as the heat of detonation of ammonium nitrate while for HBX-3 and TNT/ALEX-20 the values were taken as the 0 percent aluminium content case. Using the values of the heat of detonation given Table 4 the calculated *C-J* parameters compared quite well within 8 percent of the accepted experimental values found.

The fourth class of explosives on which an attempt was made to apply the equations to is the high energy density explosive compounds. These materials have very large detonation pressures, velocities and temperatures. For this study the equations were applied to three compounds for which data could be found and these are CL-20 and two other poly-nitro-cubane compounds and two meta-stable cluster compounds. CL-20 is one of the most powerful CHNO explosives, has a density of 2.02 g/cm^3 and a heat of formation of +412 *kJ/mol* which results in a very high detonation velocity of about 9300 *m/s*. The other two poly-nitro-cubane compounds are octanitro-cubane (ONC) and a new formulation studied by Rice [13], [14] and is named here for convenience as PNCF – proposed poly-nitro-cubane formulation. These poly-nitro-cubane compounds have some extraordinary physical and chemical properties. This compound type has a heat of formation of approximately 170 *kcal/mol*. A distortion in the cubane molecule manifests itself in high strain energy of about 190 *kcal/mol*. These properties and a high density of about 1900 kg/m^3 give these compounds high detonation velocities of the order of about 9000 *m/s*. The calculated *C-J* parameters for CL-20 and the two poly-nitro-cubane compounds compare quite well, within 5 percent of the measured or predicted values obtained from the references [13] [14], [16], [18], [24], [25]. For the meta stable clusters two compounds for which data was found were chosen to calculate the *C-J* parameters. These meta-stable clusters and molecules are able to accumulate energy that is orders of magnitude larger than the usual exothermic chemical reaction. Energy accumulated in the meta-stable state is released upon transition to the stable state. In transferring to its equilibrium state, either by fusion of the clusters into a bulk sample or fission of a large cluster into small molecules or atoms energy is released. As described by Kuhl et al. [15] this is very analogous to energy release in nuclear matter. Data for two meta-stable clusters were found for the nitrogen cluster N_8 and the helium cluster He_2^+ [15]. Table 5 shows the parameters used for calculating the *C-J* parameters. The calculated *C-J* pressures compared quite well with the calculated values found in the reference [15].

The fact that the equations were able to calculate the *C-J* parameters so well for such a large range of explosive materials presents an interesting thought. Consider rewriting Equation (31) with, ΔE, the energy change as the subject of the equation to get

$$\Delta E = \left(1 - \frac{v_{CJ}}{v_0}\right)^2 D^2$$

where ΔE is in *J/kg.* If the heat of detonation is taken as the heat liberated from a completed reaction that occurs as the material is converted from a condensed state to a gaseous state then this would seem to suggest that the heat of detonation is the manifestation of the change of internal energy and is a state variable. This would imply that the path by which the compound is converted from the condensed state to the gaseous state may not necessarily need to be known in detail to calculate the *C-J* parameters and γ. It is most likely the reason why once the correct heat of detonation was obtained the equation worked well in calculating the *C-J* densities and subsequently the *C-J* pressures and $\boldsymbol{\gamma}$ regardless of the compound heterogeneity.

6. Summary and conclusions

The purpose of this work was to re-examine the shock Hugoniots while trying to define an explicit analytic solution for the Chapman-Jouguet (*C-J*) parameters for explosive compounds. In the search for this analytic solution a simple equation was obtained for the *C-J* specific density as a function of three measurable parameters, namely the density, the detonation velocity and the heat of detonation as the solid compound changes into its gaseous products. An explicit solution was obtained for the ratio of specific heats, γ, a parameter that is usually estimated from the onset. The relations developed were tested for four well studied explosive materials – PETN, HMX, RDX, TATB and very good comparisons were obtained. The equations were then tried on a broad range of explosive types such as liquid explosives, heterogeneous compounds and aluminised explosive types, and the *C-J* parameters also compared quite well with published *C-J* values. Finally, the equations were tried on advanced explosive compounds such as the poly-nitro-cubane molecular type and meta-stable clusters compounds and the *C-J* parameters obtained once more compared quite well with the published data found.

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Table 1: *A summary of relations necessary to obtain the C-J parameters*

Use of equation	Equation
Rayleigh Line, $\boldsymbol{P = f\left(\frac{v_1}{v_0}\right)}$	$P = (P_0 + \rho_0^2 D^2 v_0) - \rho_0^2 D^2 v$
C-J specific density ratio, $\frac{v_{CJ}}{v_0}$	$\frac{v_{CJ}}{v_0} = 1 - \sqrt{\frac{\Delta E}{D^2}}$
C-J Pressure, $\boldsymbol{P_{CJ}}$	$P_{CJ} = \frac{\Delta E}{v_0 - v_{CJ}} - \frac{P_0}{2}$
Specific heat capacity ratio, γ	$\gamma = 1 + \frac{P_{CJ} v_{CJ} - P_0 v_0}{\Delta E + \frac{1}{2}(P_{CJ} + P_0)(v_0 - v_{CJ})}$
Energy Hugoniot, $\boldsymbol{P = f\left(\frac{v}{v_0}\right)}$	$e - e_0 - \frac{1}{2}(P + P_0)(v_0 - v) = 0$

Table 2: *Initial values needed to obtain the C-J parameters for PETN, HMX, RDX and TATB*

Parameter	Explosive Compound			
	PETN	HMX	RDX	TATB
Loading density, ρ_o (*kg/m*^{3})	1770	1900	1800	1895
Detonation velocity, (*m/s*)	8300	9100	8750	7860
P_0 for gaseous products, (*Pa*)	101325	101325	101325	101325
P_0 for solid explosive, (*Pa*)	0	0	0	0
Specific density, $v_0 = \frac{1}{\rho_0}$ (*m*^{3}*/kg*)	5.65E-04	5.26E-04	5.56E-04	5.28E-04
Heat of detonation, $\Delta E = e_1 - e_0$, (*J/kg*)	-5794E+03	-5010E+03	-5036E+03	-3852E+03

Table 3: *Comparison of the calculated C-J parameters with published experimental data*

Chapman-Jouguet Parameter	PETN		HMX		RDX		TATB	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
$\frac{v_{CJ}}{v_0}$	0.71	0.72	0.74	0.75	0.73	0.75	0.75	0.74
ρ_{CJ} (g/cm^3)	2.49	2.45	2.52	2.52	2.42	2.41	2.52	2.56
P_{CJ} (GPa)	35.4	33.7	38.5	39.0	35.0	34.7	31.0	31.5
$\gamma = \frac{C_p}{C_v}$	2.63	2.64	3.1	3.0	2.9	2.98	3.0	----

Table 4: Density, detonation velocity and heat of detonation for a selection of explosives

Explosive Compound	Density ρ_0, *kg/m*^{3}	Detonation Velocity *D, m/s*	Heat of explosion *ΔE, kJ/kg*	Reference
LX 04	1867	8480	4360	[7], [9]
LX 10	1841	8810	5480	[7], [9]
TNT	1550	6850	4247	[1], [7], [9]
BTF	1820	8400	5800	[9], [21]
AMATOL 50/50	1550	5975	2931	[7], [9], [20]
CYCLOTOL 5/25	1760	8300	5150	[1], [7], [9]
PBX 9502	1900	7710	4180	[7], [9]
COMP B	1680	7700	5192	[1], [7], [9]
ADN	1650	5260	3535	[17], [27]
NG	1600	7600	6194	[1], [7], [9] [18]
NM	1130	6280	4440	[1], [7], [9, [18]]
TNT/ALEX - 20	1740	6850	4528	[7], [19] [20], [26]
HBX 3	1852	7300	2826	[7], [9], [23], [22]
ANFO	840	4740	1592	[1], [7], [9], [12]
CL20	1980	8800	6162	[16], [24], [25], [18]
PNCF	1770	8600	5280	[13], [14]
ONC	1980	8800	7482	[16], [18]

Table 5: *Comparison C-J parameters, γ with published experimental values*

Explosive compound	$P_{C\text{-}J}$ (GPa)		ρ_{CJ} (g/cm^3)	γ	% Difference in P_{CJ}
	Cal	Exp.	Cal.	Cal.	
LX 04	37.00	35.00	2.48	3.04	5.6
LX 10	40.00	38.20	2.49	2.84	5.9
TNT	21.90	21.00	2.22	2.55	4.2
BTF	37.50	36.00	2.54	2.65	4.3
AMATOL50/50	15.90	16.40	2.17	2.66	3.3
CYCLOTOL 75/25	33.20	32.30	2.42	2.77	2.6
PBX 9502	30.00	30.20	2.59	2.85	0.8
COMP B	30.52	29.50	2.38	2.59	3.6
ADN	16.32	16.00	2.57	2.2	2.0
NG	30.10	27.00	2.36	2.37	11.0
NM	14.90	14.40	1.70	2.32	4.2
TNT/ALEX -20	24.90	23.00	2.55	2.44	8.2
HBX 3	22.73	22.30	2.41	3.23	1.9
ANFO	5.02	5.50	1.14	2.84	8.7
CL-20	43.25	44.20	2.76	2.70	2.2
PNCF	35.00	35.00	2.42	2.83	0.0
ONC	47.66	50.00	2.87	2.48	4.7

Table 6: *Properties and **c**omparison of C-J parameters, γ with published values for Meta-stable cluster compounds* N_8 *FCC and* He_2^+

Parameter	N_8 *FCC*		$\boldsymbol{He_2^+}$	
Loading Density *kg/m*^{3}	3 186		3 164	
Heat of Detonation *MJ/kg*	28		210	
Detonation Velocity *km/s*	19.7		43	
	Calculated	Ref. Value	Calculated	Ref. Value
P_{cj} *GPa*	332	314	1 962	1 632
C-J density *kg/m*^{3}	4 357	4 266	4 784	4 423
$\boldsymbol{\gamma}$	2.82	-	2.30	-

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