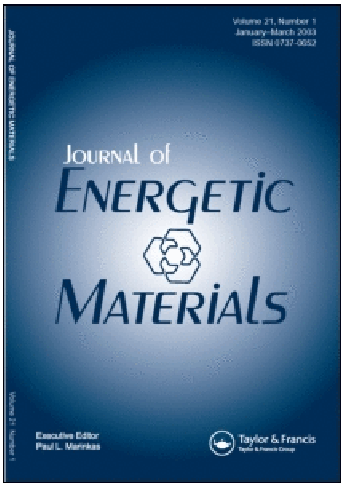

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Chemical Energy Release in Several Recently Discovered Detonation and Deflagration Flows

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Chemical Energy Release in Several Recently Discovered Detonation and Deflagration Flows

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Several recent experiments on complex detonation and deflagration flows are analyzed in terms of the chemical energy release required to sustain these flows. The observed double cellular structures in detonating gaseous nitromethane–oxygen and NO_2*–fuel (*H_2*,* CH_4*, and* C_2H_6*) mixtures are explained by the amplification of two distinct pressure wave frequencies by two exothermic reactions, the faster reaction forming vibrationally excited* NO^* *and the slower reaction forming highly vibrationally excited* N_2^{**}*. The establishment of a Chapman-Jouguet (C-J) deflagration behind a weak shock wave, the C-J detonation established after a head-on collision with a shock front, and the C-J detonation conditions established in reactive supersonic flows are quantitatively calculated using the chemical energy release of a* $H_2 + Cl_2$ *mixture. For these three reactive flows, these calculations illustrate that different fractions of the exothermic chemical energy are used to sustain steady-state propagation. C-J detonation calculations on the various initial states using the CHEETAH chemical equilibrium code are shown to be in good agreement with experimental detonation velocity*

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measurements for the head-on collision and supersonic flow detonations.

Keywords: deflagration, detonation, energy release, nonequilibrium

Introduction

Nonequilibrium Zeldovich-von Neumann-Doering (NEZND) theory identified the nonequilibrium chemical processes that precede and follow exothermic energy release within the reaction zones of self-sustaining detonation waves in gaseous, liquid, and solid explosives [1–3]. Recently, several new reactive flows were investigated experimentally. These include double cellular structures in detonating gaseous nitromethane–oxygen [4,5] and NO_2–fuel (H_2, CH_4, and C_2H_6) mixtures [6,7]; Chapman-Jouguet (C-J) deflagration behind a weak shock front [8]; C-J detonation following a head-on collision with a shock front [9,10]; and steady-state detonation conditions established in reactive supersonic flows [11]. The chemical energy release occurring in each of these reactive flows is analyzed.

Explanation of the Double Cellular Structure in Gas-Phase Detonation Waves

Sturtzer et al. [4] discussed the origin of the experimentally observed double cellular structure in gaseous nitromethane–oxygen mixtures [5]. At high equivalence ratios of nitromethane to oxygen, the secondary cells were found to be very small at the onset of the detonation cell where the shock velocity exceeds the C-J detonation velocity D_{CJ} and larger at the end of the cell where the shock velocity is less than D_{CJ}. The secondary cells exhibited higher frequencies than the main cells. Strurtzer et al. [4] postulated that this double cellular structure is caused by two distinct exothermic reactions: the conversion of NO_2 groups to NO followed by the reduction of NO to N_2. One possible reaction sequence is

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \text{ (endothermic)} \qquad (1)$$

$$NO_2 + M \rightarrow NO^* + O + M \text{ (exothermic)} \tag{2}$$

$$2NO^* + M \rightarrow N_2^{**} + MO_2 \text{ (exothermic)} \tag{3}$$

where M denotes one of several possible reactive collision partners and * denotes vibrational excitation. Because both reactions are exothermic, both NO^* and N_2^{**} are vibrationally excited and can amplify pressure wavelets and create cellular structures. Reaction (3) is approximately four times more exothermic than reaction (2) and forms highly excited N_2^{**}, which has higher vibrational quanta energies (3340 K) than NO^* (2690 K). Thus, the equilibration of N_2^{**} amplifies pressure waves more strongly per vibrational relaxation step than NO^*. Therefore, the main cellular structure created by N_2^{**} relaxation is larger than that created by NO^* relaxation, in agreement with experiments.

Desbordes et al. [6] and Joubert et al. [7] have measured similar double cellular structures for mixtures of NO_2/N_2O_4 with various fuels (H_2, CH_4, and C_2H_6). The initial exothermic step identified as the reaction:

$$NO_2 + H \rightarrow NO^* + OH \text{ (exothermic)}, \tag{4}$$

which was shown to be at least an order of magnitude faster than the subsequent reactions in which excited NO is the oxidizer in reactions such as:

$$2NO^* + C \rightarrow N_2^* + CO_2^* \text{ (exothermic)} \tag{5}$$

$$NO^* + H_2 + M \rightarrow H_2O^* + MN \text{ (exothermic)} \tag{6}$$

As for nitromethane–oxygen detonations, the NO_2/fuel mixture detonations exhibited double cellular structures with the NO^* species that amplifies the fine cellular structure and the more energetic products CO_2^*, H_2O^*, and N_2^* that amplify the larger cellular structure. The double cell structures of detonation waves with two exothermic reactions are sustained by energy transfer from vibrationally excited products to two distinct sets of pressure wavelets that propagate through the reaction zone and then strengthen the three-dimeensional shock front when they overtake each individual shock wave [1–3].

Chemical Energy Release in Chapman-Jouguet Deflagration Waves

The existence of C-J deflagrations has long been mathematically proposed but never demonstrated experimentally until recently [12]. When the transverse waves of a self-sustaining detonation wave are eliminated by acoustic absorbing tube walls, the detonation wave fails. When the wave emerges from the absorbing walls into a solid cylinder, a reactive flow is created, consisting of a weak shock wave followed by a deflagration wave that propagates at approximately half of the C-J detonation velocity D_{CJ}. This flow can exist for many tube diameters before completely failing or reestablishing a C-J detonation [12]. The chemical energy release for a weak shock followed by a deflagration wave resulting in a final state with zero particle velocity was calculated for a $H_2 + Cl_2$ gaseous mixture initially at 1 atm pressure and 300 K. The $H_2 + Cl_2$ system was chosen because its C-J detonation, chemical reaction kinetics, and nonequilibrium excitation states are well understood [1]. The CHEETAH chemical equilibrium computer code [13] was used to calculate reaction product end states with the perfect gas equation of state. Table 1 contains the calculated end states for the shock velocity of 974.5 m/s (Mach number = 3.21) that produced a C-J deflagration wave of that velocity and whose equilibrium reaction state had zero particle velocity. Also shown in Table 1 are the calculated product states for a C-J detonation wave (velocity = 1,729 m/s) and a hypothetical constant volume explosion. Figure 1 shows the various end states for these flows in pressure-specific volume space.

For a Zeldovich-von Neumann-Doering (ZND) detonation wave, the work done at the leading shock front W_s equals [1–3]:

$$W_s = (E_s - E_o) + u_s^2/2 = p_s(V_o - V_s) \tag{7}$$

Table 1
C-J detonation, constant volume explosion, and C-J deflagration of $H_2 + Cl_2$

	C-J detonation	Constant volume explosion	C-J deflagration
Initial volume (cm^3/g)	675.0	675.0	675.0
Unreacted state			
Shock velocity (m/s)	1,729	0	974.5
Shock pressure (atm)	37.41	1	11.69
Particle velocity (m/s)	1,441	0	750.5
Volume (cm^3/g)	112.5	675.0	155.1
Temperature (K)	1,871	300.0	806
Work done W_s (cal/g)	509.6	0	147.1
Enthalpy change (cal/g)	347.1	0	107.5
Reacted state			
Particle velocity (m/s)	717	0	0
Sound velocity (m/s)	1,012	1,032	974.5
Temperature (K)	3,130	3,289	3,046
Volume (cm^3/g)	395.9	675.0	675.0
Pressure (atm)	19.11	11.99	10.77
Enthalpy change (cal/g)	298.7	335.9	506.2
ΔHrx (cal/g)	411.0	335.9	440.0
Wc (cal/g)	193.8	0	79.8
$(u_s^2/2 - u_{CJ}^2/2)$(cal/g)	186.7	0	67.3
$p_{CJ} u_{CJ} V_o / D$ (cal/g)	129.5	0	0

where E_s is the internal energy, u_s is the particle velocity, p_s is the pressure and V_s is the specific volume at the von Neumann spike state. For steady-state propagation at C-J detonation velocity, this work must be equal to the sum of the work done by the piston action of the C-J state, the change in kinetic energy between the spike and C-J states, and the chemical work W_c done by the product gases expanding from the spike state to the C-J state along the Rayleigh line. Therefore, W_s can be

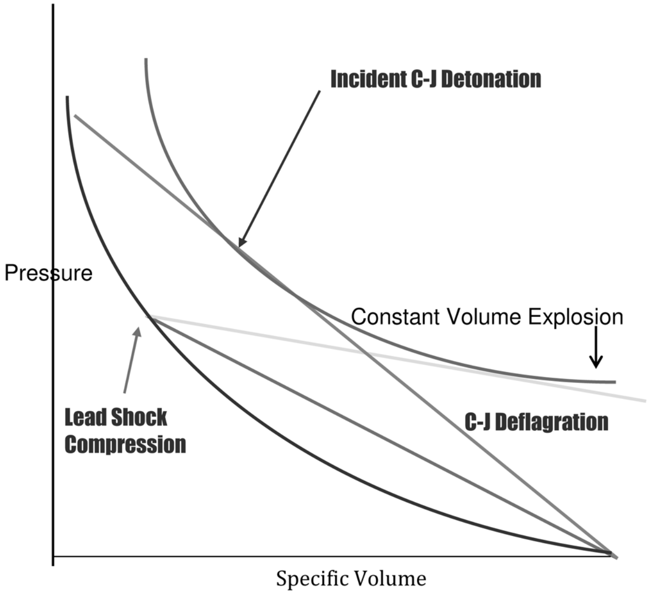

Figure 1. $H_2 + Cl_2$ C-J detonation, constant volume explosion, and C-J deflagration pressure-specific volume states.

written as:

$$W_s = p_{\mathrm{CJ}} u_{\mathrm{CJ}} V_o/D + (u_s^2/2 - u_{\mathrm{CJ}}^2/2) + W_c \tag{8}$$

where p_{CJ} is the C-J pressure, u_{CJ} is the C-J particle velocity, V_o is the initial volume, and D is the detonation velocity. The expansion work W_c is also equal to:

$$W_c = \Delta\mathrm{Hrx} - (E_{\mathrm{CJ}} - E_s) \tag{9}$$

where ΔHrx is the enthalpy of reaction and E_{CJ} is the internal energy at the C-J state. For a gamma law gas equation of state, the piston effect of the C-J state provides one quarter of W_s, the change in kinetic energy supplies 3/8 of Ws, and the chemical energy release provides the remaining 3/8 of Ws. This is shown by the values of $p_{\mathrm{CJ}} u_{\mathrm{CJ}} V_o/D$, $u_s^2/2 - u_{\mathrm{CJ}}^2/2$, and W_c listed for the $H_2 + Cl_2$ C-J detonation in Table 1. For the constant volume explosion in Table 1, no work is done and only heating due to chemical reaction occurs. For the C-J deflagration in Table 1, the initial weak shock does work ($W_s = 147.1$ cal/g), which is equal to the change in kinetic energy (67.3 cal/g) plus W_c (79.8 cal/g), because $u_{CJ} = 0$. Thus, for a C-J deflagration in $H_2 + Cl_2$, the chemical energy release provides 54% and the kinetic energy difference supplies 46% of W_s, which is much lower than the work done attaining the von Neumann spike state of a ZND detonation wave.

Detonation Following a Head-On Collision with a Weak Shock Wave

Ng et al. [9] recently reported experiments in which C-J detonations in propane–oxygen mixtures were impacted head-on by weak planar shock waves, and the transmitted detonations were described as C-J detonations. Botros et al. [10] demonstrated that similar transmitted detonations in hydrogen–oxygen and acetylene–oxygen mixtures exhibited much smaller cellular structures due to the increased density of the preshocked explosives. The planar shock waves were limited to velocities in the Mach number regime below 2, because stronger shock waves cause reactions before the detonation waves arrive. Such a head-on collision produces a reactive flow field similar to those found in the double shocked regions of the cellular structure [1], except that the particle motion following the weak shock is in the opposite direction to that produced by a detonation wave. The detonation wave must overcome this reverse kinetic energy and thus propagates at a lower detonation velocity than the original wave. This detonation wave is a C-J detonation wave with respect to the preshocked mixture and is usually called *transmitted C-J detonation.* For stoichiometric propane–oxygen mixtures at initial pressures of 0.4 atm, the measured incident C-J detonation velocity was 2,322 m/s, and the transmitted C-J velocity through a 1.65 Mach number shock was 2,083 m/s. Ng et al. [9] calculated detonation velocities of 2,318 and 2,052 m/s, respectively. CHEETAH calculated 2,327 for the incident C-J detonation and 2,071 for the transmitted C-J detonation based on the unreacted state of a 1.65 Mach number shock. Figure 2 shows the states attained in pressure–volume space.

To illustrate the chemical energy release, a ZND-type calculation was done for an $H_2 + Cl_2$ detonation wave impacting a Mach number = 2 incident shock wave (shock velocity = 606 m/s). A weak shock wave of velocity 606 m/s produces a compressed state of 4.417 atm pressure, a particle velocity of 385.7 m/s, and a shock temperature of 481 K. The resulting C-J detonation wave transmitted through this preshocked state has a calculated velocity of 1,500 m/s. This decrease in C-J detonation velocity is similar to those measured for propane–oxygen mixtures. Table 2 lists the calculated properties of a

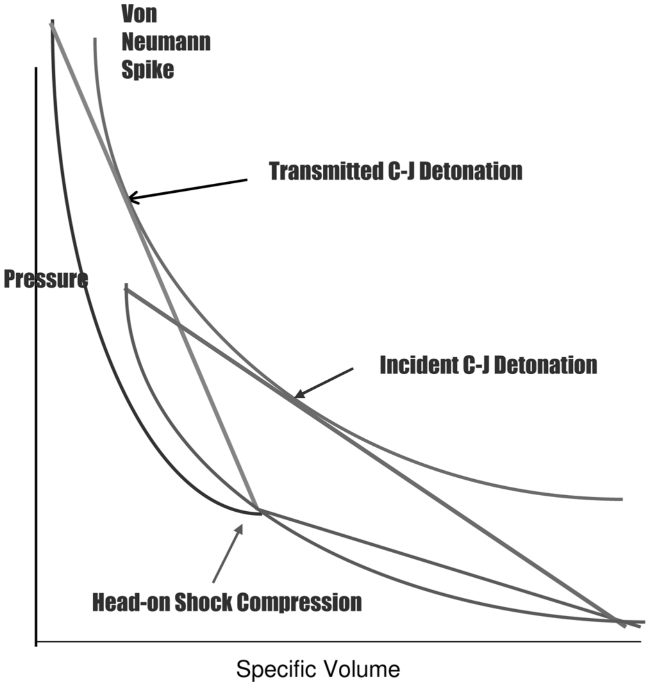

Figure 2. Incident $H_2 + Cl_2$ C-J detonation head-on collision with a weak shock and the resulting transmitted C-J detonation in pressure–volume space.

Table 2

Head-on collision of a C-J detonation with a weak shock wave in $H_2 + Cl_2$

Weak shock velocity = 606 m/s	
Shock temperature = 481 K	
Shock pressure = 4.417 atm	
Compressed volume = 245.3 cm^3/g	
Particle velocity = − 385.7 m/s (opposite direction from incident detonation wave)	
Work done $W_s = 46.0$ cal/g	
Incident C-J detonation wave properties (see Table 1)	
Transmitted detonation wave velocity = 1,500 m/s	
Von Neumann spike:	Temperature = 1641 K Pressure = 77.39 atm Particle velocity = 1,208 m/s (net particle velocity = 822.3 m/s) Volume = 47.79 cm^3/g Total work done $W_s = 370.1 + 46.0 = 416.1$ cal/g
C-J state:	Temperature = 3400 K Pressure = 40.70 atm Volume = 147.0 cm^3/g Particle velocity = 611 m/s Sound velocity = 889 m/s ΔHrx = 419.3 cal/g Enthalpy change = 419.4 cal/g $(u_s^2/2 - u_{\mathrm{CJ}}^2/2) = 128.9$ cal/g $p_{\mathrm{CJ}} u_{\mathrm{CJ}} V_o / D = 100.8$ cal/g $W_c = 186.4$ cal/g

transmitted C-J $H_2 + Cl_2$ detonation wave into a 606 m/s head-on shock wave. The calculated chemical energy release W_c supplied 44.8% of the total W_s, the change in kinetic energy 31%, and the piston motion of the C-J state 24.2%. To make up for the initial opposing particle flow, the chemical energy release supplied a greater fraction of the overall work than in an incident C-J detonation wave, whose corresponding values are listed in Table 1.

Gaseous Detonation Waves in Reactive Supersonic Flows

Vasil'ev et al. [11] recently measured the detonation velocities in hydrogen–air mixtures of various concentrations that propagated either into or in the same direction as supersonic flows of the inert mixture. They reported data on supersonic flows with Mach numbers up to 4. When a detonation wave propagated head-on into a supersonic flow, the transmitted detonation velocity was measured to be less than the incident C-J velocity. The effect was similar to that discussed previously for the collision of a detonation wave with a head-on weak shock wave. When the detonation wave propagated in the same direction as the supersonic flow and overtook it, the resulting transmitted detonation wave velocity was greater than the incident C-J velocity. In the head-on case, the initial supersonic flow is in the opposite direction, and the leading shock of the incident detonation wave does more work on the unreacted gases to force them to propagate in the direction of the shock front than it would in a stationary mixture. In the overtake case, the unreacted gases are already moving in the direction of the detonation wave front, and therefore the leading shock front does less work in accelerating the gases to the correct unreacted particle velocity. Thus, the initial particle velocity acts like an endothermic process in the case of a head-on collision and like an exothermic process in case of the incident detonation wave overtaking the supersonic flow.

CHEETAH calculations produced detonation velocities of 1,976 m/s for a 1 atm stationary H_2 + air stoichiometric mixture, 2,065 m/s for the detonation overtaking a Mach number 4 flow with an initial velocity 1,600 m/s, and 1,864 m/s for the detonation colliding head-on with a Mach number 4 supersonic flow that had an initial flow velocity of 1,600 m/s. These calculated detonation velocities agree very closely with those measured by Vasil'ev et al. [11]. Comparing the detonation velocity decreases for the cases of head-on shock and head-on supersonic flow, the detonation velocity decrease was greater for the head-on shock case, because the shock increases the density and temperature of the gas as well as accelerates it. The increased density and temperature cause the overall chemical energy release to be less exothermic than in the incident C-J detonation wave and in the transmitted C-J detonation than is produced by head-on supersonic flow. Figure 3 shows

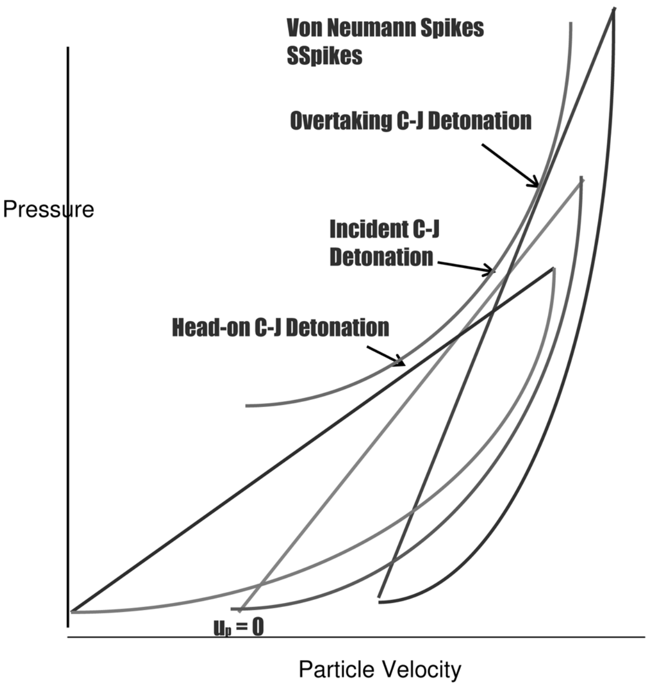

Figure 3. Incident $H_2 + Cl_2$ C-J detonation head-on collision and overtaking supersonic flows with the resulting transmitted C-J detonations in pressure–particle velocity space.

Table 3

Transmitted $H_2 + Cl_2$ detonation states for opposite and same direction supersonic flows

	Opposite direction	Same direction
Initial particle velocity (m/s)	−1,212	1,212
Initial kinetic energy (cal/g)	−175.5	175.5
Incident detonation wave (see Table 1)		
Transmitted detonation velocity (m/s)	1,571	1,850
Unreacted states		
Shock pressure (atm)	30.81	42.91
Shock temperature (K)	1,606	2,091
Volume (cm^3/g)	117.3	109.6
Particle velocity (m/s)	1,298	1,555
Total work done W_s (cal/g)	$416.0 + 175.5 = 591.5$	$587.4 - 175.5 = 411.9$
C-J product states		
Pressure (atm)	16.18	21.99
Temperature (K)	2,810	3,500
Volume (cm^3/g)	390	392
Particle velocity (m/s)	663	784
Sound velocity (m/s)	908	1,066
ΔHrx (cal/g)	516.6	342.2
Enthalpy change (cal/g)	283.4	344.4
$p_{\mathrm{CJ}} u_{\mathrm{cj}} V_o / D$ (cal/g)	111.6	152.3
$(u_s^2/2 - u_{\mathrm{CJ}}^2/2)$(cal/g)	148.8	216.5
W_c (cal/g)	330.8	42.8

the states attained in these supersonic flow detonations in pressure–particle velocity space.

Table 3 shows the chemical energy release calculations for $H_2 + Cl_2$ subjected to opposite and same direction supersonic flows with initial velocities of Mach number 4 (1,212 m/s). The calculated detonation velocities in Table 3 (1,729 m/s for C-J detonation, 1,850 m/s for detonation overtaking a supersonic flow, and 1,571 m/s for head-on interaction with a supersonic flow) agree closely with CHEETAH $H_2 + Cl_2$ C-J detonation velocity calculations (1,721, 1,846, and 1,570 m/s, respectively). These calculated detonation velocity increases/decreases for $H_2 + Cl_2$ are similar to those measured and calculated for H_2 + air mixtures. The calculated changes in kinetic energy differences, overall heats of reaction, and the work done at the shock front in these supersonic flows are listed in Table 3. Due to the large kinetic energy of the supersonic unreacted explosive mixture, the percentage of work done by the chemical energy release W_c is much higher (55.9%) in the case of opposite direction flow than in the case of same direction flow (10.4%). This difference is balanced by a larger fraction of W_c furnished by the change in kinetic energy (52.6% versus 25.2%) and by the piston effect of the C-J state (37.0 versus 18.9%) for the same direction supersonic flow case versus the opposite direction case.

Conclusions

Pressure wave amplifications involving two vibrational deexcitation energies and rates following two separable exothermic reactions were shown to be consistent with the double cellular structure observed experimentally in gaseous nitromethane–oxygen and NO_2–fuel mixtures [4–7]. The two frequencies of the double cellular structure waves and the resulting cell sizes correlate well with the vibrational energies of excited NO^* for the first, less exothermic reaction and of excited N_2^{**} for the second, more exothermic reaction.

Chemical energy release calculations for $H_2 + Cl_2$ mixtures were done to illustrate four recently measured reactive flows: a weak shock followed by a C-J deflagration; the head-on collision of a C-J detonation wave and a weak shock; the head-on collision of a C-J detonation wave and a supersonic flow; and the overtake of a supersonic flow by a C-J detonation wave. In the C-J deflagration case, all of the chemical energy is required to attain the sonic state with zero particle velocity at the initial density of the explosive mixture. Thus, no excess chemical energy [1] is available to amplify the weak leading shock front, which therefore cannot accelerate to detonation. The head-on collision of a C-J detonation with a weak shock wave or a supersonic flow is shown to result in a transmitted C-J detonation at a lower velocity, because the negative particle velocity and, in the case of the weak shock, the higher density and temperature cause a lower chemical energy release. In the case of a C-J detonation wave overtaking a supersonic flow, the transmitted detonation wave has a higher detonation velocity than the original detonation wave. This is due to the fact that the initial particle velocity is in the same direction of the detonation flow, which then has to do less work to accelerate the moving gases to the correct unreacted particle velocity. The transmitted detonation wave then has a greater portion of its chemical energy release available to support a faster C-J detonation velocity. These transmitted C-J detonation waves propagate steadily for relatively long distances at velocities very close to calculated C-J values calculated by CHEETAH and other methods [8–11,13]. Thus, they are self-sustaining C-J detonation waves with respect to their imposed initial conditions.

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