On the Origin of the Double Cellular Structure of Detonation In Gaseous Nitromethane

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Abstract

An experimental study of the detonation in gaseous nitromethane (*NM*) pure and mixed with oxygen has exhibited unambiguously the existence of a double cellular structure in the range of equivalence ratio Φ from 1.3 to 1.75 (pure *NM*). Calculations of the reaction zone of the detonation in the same range of equivalence ratio, using a detailed chemistry in the *ZND* frame, demonstrate that the chemical energy is released in two main successive reaction steps characterized by their own induction length. This work shows that these two main exothermic reaction steps, through their induction length, justify the two levels of cellular structure.

To our knowledge, this work is the first which deals with the problem of non monotonous chemical energy release behind the leading shock of a detonation wave. Results obtained strengthen the idea that the cellular detonation structure find its origin in instabilities amplified by the local high energy release rate inside the reaction zone.

1 – Introduction

Pure nitromethane (*NM*) of chemical formula $CH_3\ NO_2$ ($\Phi = 1.75$) can support by itself deflagration and detonation. It belongs to the class of monopropellant. Unlike the condensed phase, its gaseous detonation has not been widely studied.

A few years ago, detonation experiments were undertaken (Presles et al /1/) in gaseous nitromethane, and its mixtures with oxygen. Experiments show unambiguously that a double cellular structure of the self sustained detonation exists for $1.3 \leq \Phi \leq 1.75$.

The double cellular structure consists in :

- a main cell structure similar to that of detonation in classical C_nH_m/O_2 or Air mixtures.
- a net of secondary cells of basically the same shape but smaller size, present all along the main cell and particularly distinguishable in its second part. This cellular net is entirely submitted to the local detonation regime inside the main cell, i.e. the cell is very fine at the beginning of the main cell where $D/D_{CJ} > 1$ and increases in size at the approach of the apex where $D/D_{CJ} < 1$.

These observations led the authors /1/ to propose an assumption to explain the origin of the double cellular structure i.e. : “since in classical mixtures the cell size is representative of the chemical induction length, by analogy, in the case of *NM* and rich *NM/O2* mixtures we can assume that the double cellular structure could be associated with two characteristic chemical lengths during the process of heat release and the chemistry could be thought to proceed through two main steps”.

In this paper, in order to validate this assumption, 1D calculations of the reaction zone in the frame of the *ZND* model have been carried out using a detailed chemical kinetics of *NM* decomposition and oxidation.

2 – The classical cellular structure of detonation

Since the discovery of Denisov and Troshin in 1959 /2/ the detonation wave appears as a 3D periodic unsteady structure of shocks and combustion waves, more complex than the ideal models of detonation (*CJ* and *ZND*).

The basic 3D structure consists in a cell representative of periodic collisions of triple points. Inside a cell, the detonation velocity is continuously decreasing and is quasi *CJ* at the middle of the cell. Simultaneously a progressive decoupling between the leading curved shock and the flame takes place all along the cell. Whatever the reactive mixture and the detonation regime, the shape of the cells is conservative (the ratio of cell width λ over cell length L is a constant of about 0.6).

According to Schelkhin and Troshin /3/, the cell size λ varies as the chemical induction length L_i of the single exothermic step behind the shock wave. Usually λ is one or two orders of magnitude larger than L_i.

An unsteady sub-cellular structure can be observed in the first half of the main detonation cell for reactive mixture whose reduced global activation energy E_a/RT_{ZND} is larger than 6. According to Manzhaleï /4/, this sub-structure has the same origin as the main cell and as its size is exponentially dependent on the local detonation velocity the size of this sub-structure increases up to the middle of the main cell where $D \cong D_{CJ}$ and then disappears.

3 – The cellular structure of nitromethane

Examples of detonation cellular structure of *NM* and *NM/O2* mixtures are displayed in Fig. 1 and Fig. 2 respectively for spinning and multiheaded detonations, where two nets of cellular structures can be observed. In these cases, unlike the classical reactive mixtures, the cellular structure of small size, named in the following secondary cellular structure, is present everywhere.

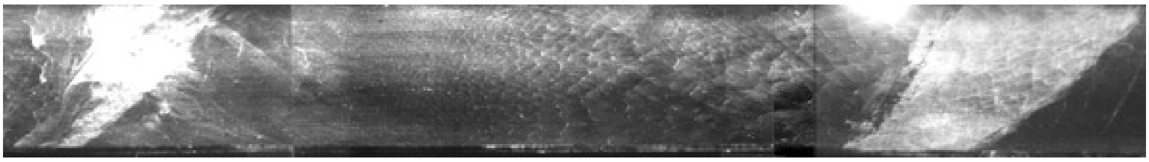

Fig. 1: Spinning detonation cellular structure of *NM* (P_0=0.4bar, T_0=390K**,** Φ=1.75)

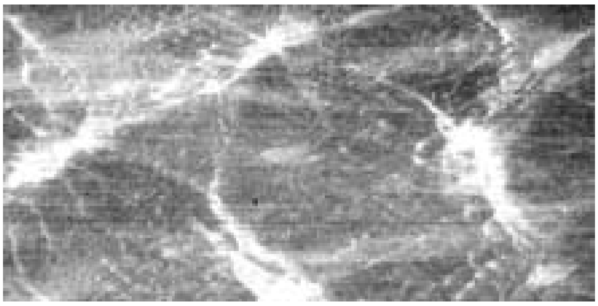

Fig. 2: Multiheaded detonation cellular structure of *NM/O2* mixture (P_0=0.8bar, T_0=390K**,** Φ=1.4)

The size of this secondary cellular structure, as previously explained, increases continuously all along the main cell according to the local detonation velocity. λ_1 is the size of the secondary cellular structure measured in the middle of the main cell, where $D \cong D_{CJ}$, and λ_2 is that of the main cell. The experimental values of λ_1 and λ_2 versus Φ, in the range $0.1 \leq \Phi \leq 1.75$, are presented in Fig. 3. For pure *NM* λ_2 is more than 2 orders of magnitude larger than λ_1 .

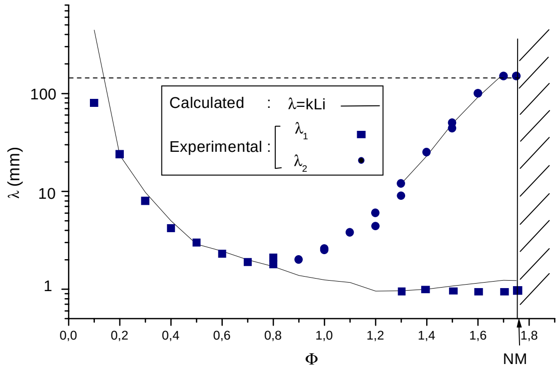

Fig. 3 : Calculated and experimental cell size λ versus the equivalence ratio Φ.

Adding oxygen, in the range $1.3 \leq \Phi \leq 1.75$, the size λ_2 drops strongly, λ_1 remaining quasi constant. For $\Phi = 1.3$ λ_2 is only one order of magnitude larger than λ_1. Below $\Phi = 1.3$, no secondary cellular structure can be seen in the main cell.

4 - Numerical study of the reaction zone of the detonation wave.

According to our previous assumption, each main reaction step of the chemical energy release should be characterized by its own induction time and length. In order to check this assumption we performed 1D calculations of the reaction zone of the self sustained detonation wave in gaseous *NM* and mixtures *NM/O2* for $0.1 \leq \Phi \leq 1.75$, in the frame of the *ZND* model using a detailed chemical scheme of *NM* decomposition and oxidation /5/. Chemical equations are solved using CHEMKIN code (/6/ and /7/) along the Rayleigh-Michelson line from the *ZND* state towards the *CJ* one. Measured values of the detonation velocity being close to calculated ones (D_{CJ}) proves that all the chemical energy is released inside the reaction zone in accordance with the *CJ* assumption which justify the above calculations. Finally one has to recall that the thermal state (P,T…) and the composition of chemical species depends on the scheme of the chemical kinetics used.

Analysis of the evolution of the temperature inside the reaction zone shows two different trends depending on whether the value of the equivalence ratio is higher or smaller than 1.3.

Examples of time evolution of the temperature inside the reaction zone representative of these different trends are displayed in Fig. 4 and 6. They both show that the temperature undergoes from the *ZND* state large negative and positive variations up to the *CJ* state.

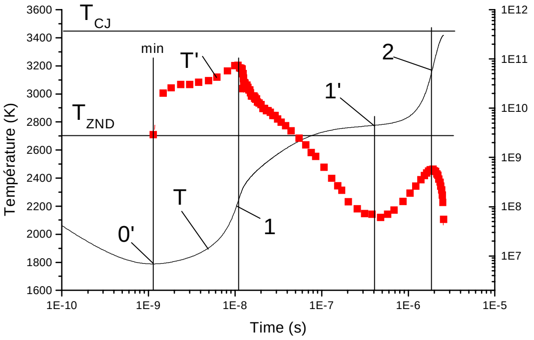

Fig. 4 : Time evolution of the temperature T and of its derivative T' for the mixture *NM/O2* (P_0=0.3bar, T_0=363K, Φ=1.5)

The complete thermal evolution of the case presented in Fig.4 between *ZND* and *CJ* states is displayed in a (P,v) diagram (Fig. 5) where the successive phases are identified with numbers 0',1,1',2.

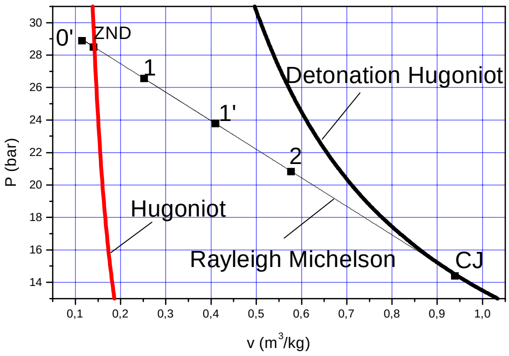

Fig. 5 : Evolution of the thermal state between *ZND* and *CJ* states for the mixtures *NM/O2* (P_0=0.3bar, T_0=363K, Φ=1.5)

The 1^{st} reaction step (*ZND* to 0') is very fast (order of a nanosecond), endothermic and corresponds to breaking of the C-N link. Temperature decreases from the *ZND* value (2700K) to a minimum of about 1800K.

The 2^{nd} reaction step (0’ to 1’) is exothermic and temperature increases to an intermediate value ($T_{1'}$≈2800K) which is close to the *ZND* one. In this reaction step, NO_2 is converted into *NO.*

The 3^{rd} and final reaction step (1’ to *CJ*) is also exothermic and leads to the *CJ* state. During this step (order of 1µs) the oxidizer *NO* is completely consumed.

The two inflexion points on the temperature curve corresponding to local maxima of heat release rate (i.e. $\frac{dT}{dt}$ max) during the two main exothermic chemical reactions are used to define two induction times:

1. τ_{i1} between the time origin (*ZND*) and the first inflexion point. This induction time is defined whatever the equivalence ratio of the *NM/O2* mixture.
2. τ_{i2} between the time origin and the 2^{nd} inflexion point which exists only for $\Phi \geq 1.3$ and is at least more than one order of magnitude larger than τ_{i1}.

When Φ decreases from 1.3 to 1, τ_{i1} remains nearly constant and the absence of a second inflexion point prevents, according to our criteria, to define a second induction time even if part of the chemical energy is released in continuity of the first one (see Fig. 6).

For the lean mixtures also only one induction time can be determined.

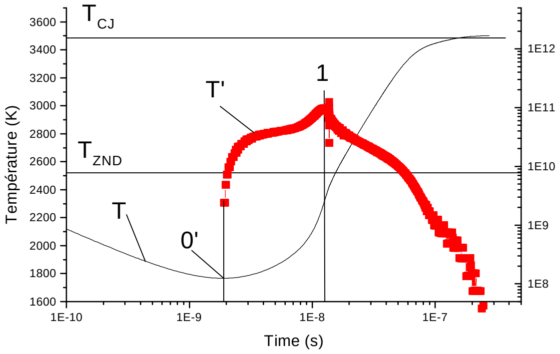

Fig. 6: Time evolution of the temperature inside the reaction zone of the detonation of the mixture *NM/O2* (P_0=0.3bar, T_0=363K, Φ=1)

Induction lengths L_{i1} and L_{i2} are obtained by integration of the particle velocity during each induction time in the range $0.1 \leq \Phi \leq 1.75$ (Fig. 7). In accordance with what has been previously said, only one induction length remains for Φ<1.3**.**

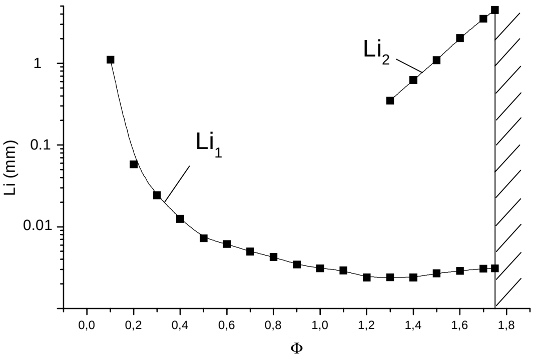

Fig. 7: Calculated induction lengths L_{i1} and L_{i2} for the mixture *NM/O2* with respect to the equivalence ratio Φ (P_0=0.3bar, T_0=363K).

The calculated values of the cell sizes λ_1 and λ_2 from the induction lengths L_{i1} and L_{i2} by means of the correlation $\lambda_j = k_j L_{ij}$ (j=1,2) have been reported on Fig. 3 (full lines). The values of k_1 and k_2 (respectively 400 and 50) were adjusted to obtain the best fit with the experimental λ(Φ) data.

Conclusion

Previous experimental observations of the detonation structure of gaseous *NM* and *NM/O2* mixtures revealed the existence of a double cellular structure for $1.75 \geq \Phi \geq 1.3$. Calculations of the reaction zone in the *ZND* model using a detailed chemical scheme for the *NM* decomposition and oxidation show that chemical energy is released in two main reaction steps on this range of equivalence ratio, leading to the definition of two different induction lengths.

The comparison of experimental and numerical results confirm our assumption on the origin of the double cellular structure i.e. that the two cellular structures are explained by a chemical heat release through two main reaction steps. To our knowledge this study is the first which deals experimentally and numerically with a non monotonous chemical heat release inside the reaction zone of a detonation wave and reinforces the idea, developed and checked with classical reactive mixtures, that the cellular structure of the detonation is the consequence of local high chemical heat release rate of Arrhenius type.

References :

/1/ Presles H.N., Desbordes D., Guirard M., Guerraud C., Gaseous nitromethane and nitromethane-oxygen mixtures : a new detonation structure, Shock Wave, 6, 111-114, 1996.

/2/ Denisov Yu.N., Troshin Ya.K., On the mechanism of detonation combustion, 8th Symposium (International) on Combustion, Williams and Wilkins, Baltimore, p 600-606, 1962.

/3/ Schelkhin K.I., Troshin Ya.K., Gazodynamika Gorenyia, Moscow, 1963.

/4/ Manzhaleï VI, On the fine structure of gaseous detonation front, FGIV 3, 470, 1977.

/5/ Djebaili – Chaumeix N., Abid S., Paillard C.E., Shock tube study of the nitromethane decomposition and oxidation, 21st Symposium on Shock Waves, 1, p 121-126, 1997.

/6/ Kee R.J., Rupley F.M., Miller J.A. : The Chemkin thermodynamic data base. Sandia Report, SAND87-8215B, UC-4, 1993.

/7/ Kee R.J., Rupley F.M., Miller J.A. : Chemkin-II : A Fortran chemical kinetics package for the analysis of gas phase chemical kinetics. Sandia Report, SAND89-8009B . UC-706, 1994.