Numerical Study of Detonation Propagating in Hydrogen-Nitrogen Tetroxide Mixtures

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1 Introduction

Detonations propagating in hydrogen-nitrogen tetroxide (H_2-NO_2/N_2O_4), potentially diluted with various amounts of argon, demonstrate unique features compared to detonation propagating in most common fuel-oxidizer mixtures [1]. For lean to stoichiometric compositions, the chemical heat release is driven by a main exothermic step and the cellular structure exhibits a classical single cellular detonation structure. For rich mixtures, the chemical heat release is separated into two steps, which results in the appearance of a double cellular structure featuring two superimposed cellular networks with characteristic sizes one order of magnitude apart. Detonations propagating in H_2-NO_2/N_2O_4 mixtures have been studied both experimentally and numerically [1–7].

Focusing on the available numerical studies, we note that Guilly et al. [3] were the first to determine the critical conditions for the double cellular structure to be numerically reproduced in a two-dimensional framework. Using a two-step reaction model, they showed that the second reaction must have a rate several orders of magnitude lower than the rate of the first reaction for the two intricated networks of cell to be obtained. Virot et al. [4] studied numerically the three-dimensional structure of detonation driven by two, successive exothermic steps. As the tube diameter was progressively decreased, they observed the transitions from double cellular structure to spinning double structure to single cellular structure to spinning single structure. Still relying on a two-step reaction model, Virot et al. [5] further demonstrated the existence of low-velocity detonation supported by only the first step of heat release when losses were introduced in the two-dimensional simulations. The study of Sugiyama and Matsuo [6] also relied on a globalized two-step model. They could reproduce the double cellular structure as in Guilly et al. [3], and they showed that a detonation with double cellular structure could be divided between a primary and a secondary detonation. In this framework, both detonations demonstrate a single step of heat release, and a hypothetical intermediate initial state is defined. The first and only study relying on detailed chemistry was conducted by Davidenko et al. [7]. Based on the mechanism from Joubert et al. [1, 12], they developed a reduced reaction model for rich mixtures with $\Phi = 1.5$, that includes 20 reactions and 17 species. It was demonstrated that the chemical sequence, H+NO=OH+N followed by N+NO=N_2+O, has a predominant impact on the appearance of the double cellular structure. From the above literature review, we note the following limitations in the existing literature: (i) only a limited number of numerical investigations were conducted; (ii) all of them, except one, were performed with a globalized two-step reaction model; (iii) the simulations were performed for a limited range of compositions, basically rich mixtures for which the two-step heat release feature is well pronounced; (iv) none of these studies investigated in detail the dynamics of the double cellular structure. Therefore, the goal of the present study was to study through two-dimensional numerical simulations performed with realistic chemistry the structure and dynamics of detonation in H_2-NO_2/N_2O_4 mixtures over a wide range of equivalence ratio. The paper is organized as follows: in section 2, we present the governing

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equations and numerical approach we employed; in section 3, we introduce the new reduced reaction model we developed to study a wider range of conditions; in section 4, we study in details the structure and dynamics of detonation in H_2-NO_2/N_2O_4 mixtures of various equivalence ratio; in section 5, we provide concluding remarks.

2 Governing equations and numerical approach

This study considers the detonation of gas mixtures in two-dimensional, planar channels. The problem is ruled by the reactive Euler equations. The conservation of mass, momentum, energy, and species k can be written in compact form as

$$\frac{\partial \mathbf{Q}}{\partial t} + \frac{\partial \mathbf{F}}{\partial x} + \frac{\partial \mathbf{G}}{\partial y} = \mathbf{S} \tag{1}$$

with $\mathbf{Q}$ the vector of conservative variables, $\mathbf{F}/\mathbf{G}$ the convective flux in the x/y direction, and $\mathbf{S}$ the source term. They read

$$\mathbf{Q} = \begin{bmatrix} \rho \\ \rho u \\ \rho v \\ \rho E \\ \rho Y_k \end{bmatrix} \quad \mathbf{F} = \begin{bmatrix} \rho u \\ \rho u^2 + p \\ \rho uv \\ \rho uE + pu \\ \rho u Y_k \end{bmatrix} \quad \mathbf{G} = \begin{bmatrix} \rho v \\ \rho uv \\ \rho v^2 + p \\ \rho vE + pv \\ \rho v Y_k \end{bmatrix} \quad \mathbf{S} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ \rho \dot{\omega}_k \end{bmatrix} \tag{2}$$

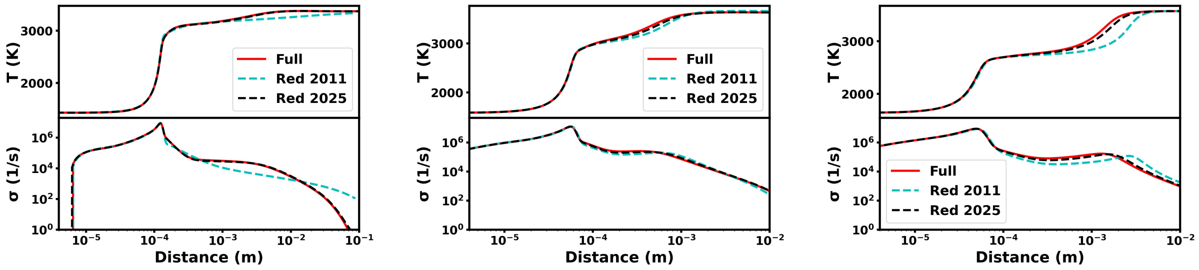
where ρ is the density, (u,v) are the velocity components, Y_k is the mass fraction of the k^{th} species, and E is the total energy. The ideal gas law is assumed, i.e., p=$\rho RT/\bar{W}$, with $\bar{W}$ the mixture molar mass and T the temperature.

The equations are solved using a finite volume technique on block-structured grids. The numerical fluxes are estimated at cell edges using the HLLC Riemann solver [8]. High-orders in space and time are achieved by a fifth-order WENO scheme [9] and third-order Runge-Kutta method [10], respectively. An adaptive mesh refinement (AMR) strategy is employed to finely resolve the induction zone or small structures and is based on the Sun-Takayama criterion [11] applied simultaneously to pressure, density, OH mass fraction, and NO mass fraction. The maximum level of refinement corresponds to a minimum grid spacing of 3 μm, providing an effective resolution in the ranges 17 to 41 and 186 to 1112 points/Δ_i, respectively for the first and second steps of heat release. The geometry considered is a channel with an upper adiabatic slip wall and lower symmetry axis. Extrapolation is used at both tube ends. The channel height h is fixed at 26 mm, which is the tube radius used in the experiments of Joubert et al. [1]. For a given mixture, the solution of a 1D simulation is mapped onto the actual 2D channel geometry with slight disturbances in the fresh mixture ahead of the shock (two small square zones with ± 10 % change in the concentration), so as to trigger the development of transverse waves. Recognizing that the simulated detonations with double cellular structure are expected to be mode-locked, we noted that this is likely also the case in the experiments. The typical simulation time was approximately 4 days on 150 processors.

3 Reaction mechanism

We investigated two-dimensional detonation in H_2-NO_2/N_2O_4 mixtures with different equivalence ratios, Φ = 0.5, 0.9, 1, 1.2, and 1.5. Given the high computational cost of such numerical simulations, it is needed to use a reaction mechanism as small as possible, as done in the study of Davidenko et al. [7]

for a mixture with Φ=1.5. We employed the same approach as the one used by Davidenko et al. [7] to obtain a reduced reaction model valid over an extended range of composition. Figure 1 shows the steady detonation structures, i.e., the Zeldovich-von Neumann-Doering (ZND) solutions, calculated using the full reaction model [1, 12], the reduced reaction model developed by Davidenko et al. [7] (Red 2011), and the new reduced mechanism (Red 2025) presently obtained. Red 2011 provides reasonably accurate temperature and thermicity profiles for an equivalence ratio as low as $\Phi = 0.9$. However, for $\Phi = 0.5$, the chemical heat release dynamics is not well captured. Red 2025, which includes 47 reactions and 21 species, provides accurate temperature and thermicity profiles for all equivalence ratios. Therefore, it was selected to perform the two-dimensional numerical simulations. Using Red 2025, the reduced activation energy (θ) was calculated for each step of heat release, see Tab. 1. We note that this approach has not been applied before to cases with two steps of heat release. Nevertheless, it could provide important insights to study the double cellular structure. In general, θ_1, associated with the first exothermic step, decreases as Φ is increased from 0.5 to 1.5. The behavior of θ_2, associated with the second exothermic step, is more complex and depends on the reactor model used for the computation. Nevertheless, the values of θ_2 are always lower than those of θ_1.



a) $\Phi = 0.5$ b) $\Phi = 0.9$ c) $\Phi = 1.5$

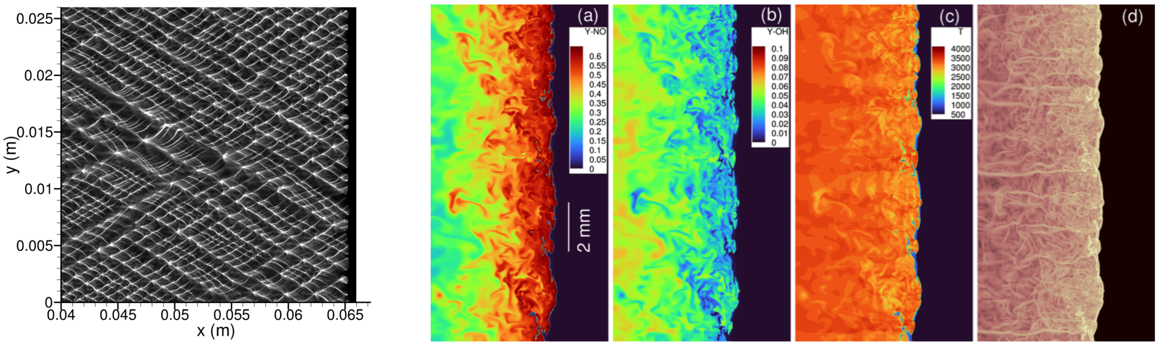
Figure 1: Temperature and thermicity profiles obtained with the full and reduced reaction models for ZND detonation propagating in H_2-NO_2/N_2O_4 mixtures with different equivalence ratios.

Table 1: Reduced activation energy calculated by considering the ZND, the constant-pressure (CP), and constant-volume (CV) reactor models. Each step of heat release was considered for H_2-NO_2/N_2O_4 mixtures with equivalence ratios.

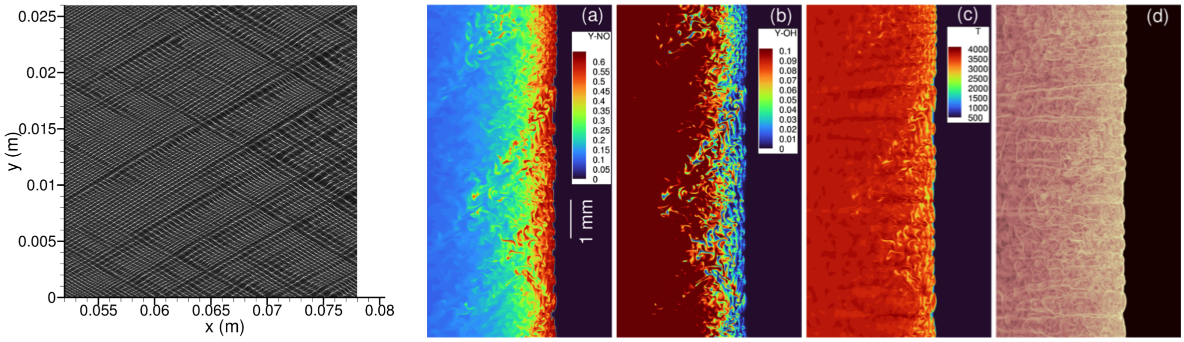
	ZND		CP		CV	
Φ	θ_1	θ_2	θ_1	θ_2	θ_1	θ_2
0.5	10.91	-	9.55	-	10.36	-
0.9	9.96	8.74	8.58	6.66	9.00	-
1	9.41	8.24	8.40	6.24	8.75	6.60
1.2	9.43	8.95	8.14	6.02	8.31	5.63
1.5	9.07	8.81	7.90	6.18	7.89	5.00

4 Detonation structure and dynamics

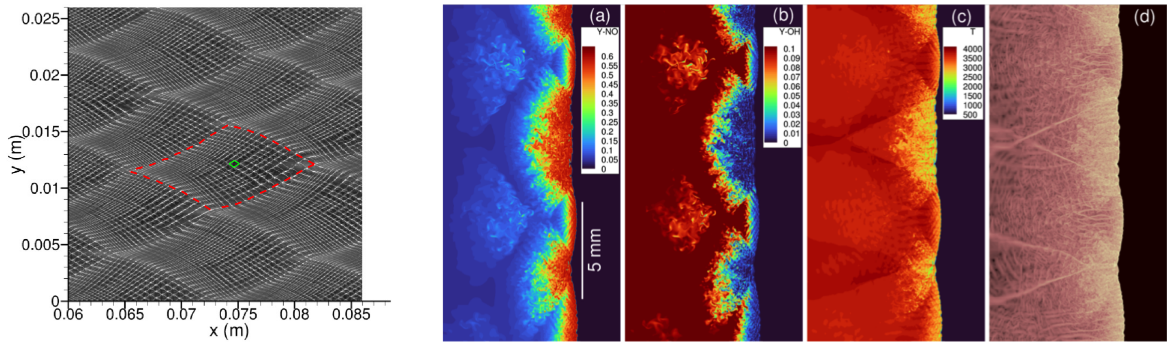
Figure 2 shows the numerical soot foils, as well as the simulated fields for several quantities. From the soot foils and the schlieren images, it is clear that the simulations predict the existence of a single cellular structure for mixtures with $\Phi \leq 1$, and of a double cellular structure (see red and green lines in the left bottom figure) for mixtures with $\Phi \geq 1.2$, which is consistent with the experimental observations of Joubert et al. [1]. Since the second step of heat release is progressively strengthened, the transition from a single to a double cellular structure should be interpreted as the appearance of a super-cellular



a) $\Phi = 0.5$



b) $\Phi = 0.9$

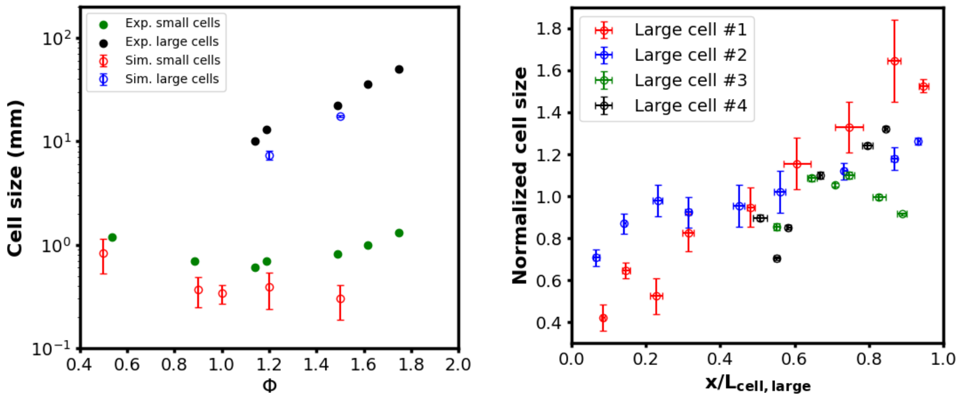


c) $\Phi = 1.2$

Figure 2: Soot foils, and fields of Y_{NO}, Y_{OH}, temperature, and density gradient for detonation propagating in H_2-NO_2/N_2O_4 mixtures with different Φ. Left and right images not at the same scale.

structure onto a cell network of much smaller size. For $\Phi = 0.5$, the cellular structure appears quite irregular, whereas for $\Phi = 0.9$ and 1.2, the cell network becomes rather regular. This is consistent with the decrease of θ as Φ increases. The instantaneous fields of Y_{NO} and Y_{OH} were chosen because of their important role as intermediate species. For the two lean mixtures, the NO field is characterized by a more or less thick layer of high mass fraction located just behind the detonation front. On the contrary, OH radicals are formed away from the front. For the rich mixture with $\Phi = 1.2$, the shape of the Y_{NO} and Y_{OH} flow fields are strongly modified and both demonstrate prominent keystone features associated with the large Mach reflection structures. In all cases, it seems that there is no region in which high concentrations of NO and OH are simultaneously present, which indicates that these two radicals are mainly formed in two successive steps. This aspect is particularly obvious for the rich mixture for which the flow fields of NO and OH appear as negatives of each other. The temperature fields show that the maximum temperature increases with Φ as the mixtures become richer and richer. For the $\Phi = 0.5$ and 0.9 cases, pockets with lower temperature, representative of partially burnt gas, are present away from the detonation front. For the mixture with $\Phi = 1.2$, the low-temperature regions are rather associated with the induction zones behind the incident shocks of the super cellular structure.

Using the numerical soot foils we obtained for mixtures with various equivalence ratios, as well as the experimental data of Joubert et al. [1], we made a comparison of the numerical and experimental cell widths / sizes associated to each cell network. For conditions for which a double cellular structure exists, the size of the small cells was extracted in the middle of the large cell, as done in the experiments. The results are shown in Fig. 3 a). The evolution of the cell size with Φ is qualitatively captured for both networks. Quantitatively, the ratio between numerical and experimental cell size is in the range of 1.6-2.8 for cells associated with the first exothermic step. For these cell sizes, the standard deviation can be as high as 40%. The cell sizes ratio ranges between 1.38 and 1.63 for cells associated with the second exothermic step. Differences between numerical and experimental cell sizes are often of a factor of two or higher and can be related to various aspects such as extrapolation of chemical kinetics, boundary conditions, geometrical constraints, and vibrational non-equilibrium [13]. In addition, we have also studied the variation of the small cell size with respect to its position within a large cell of length L for a mixture with $\Phi = 1.2$. The results are shown in Fig. 3 b), where the average cell size has been used for normalization. The size of the small cells increases significantly, between a factor of 2 and 4, along the length of the large cell. It is noted that the standard deviation, shown as error bar, can be locally very large, which is consistent with the relatively high reduced activation energy under such conditions, see Tab. 1. The corresponding experimental cell sizes may demonstrate a relatively consistent increase along L, see black symbols, or a decrease, see green symbols.

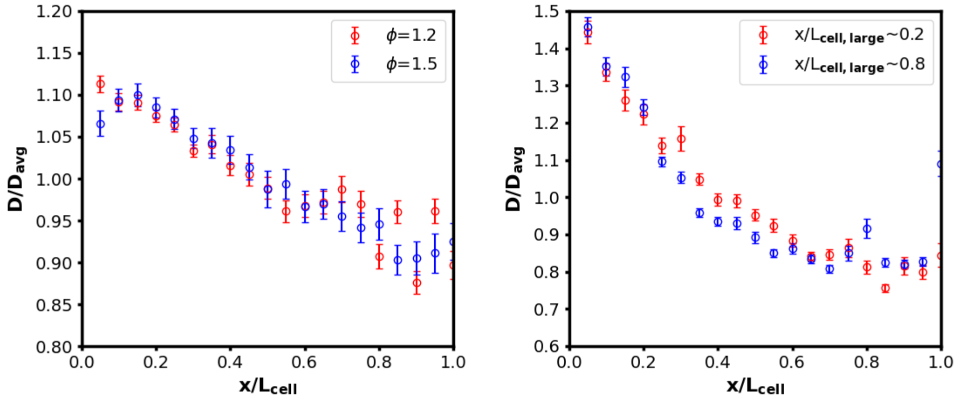


a) Large and small cell size

b) Small cell size variation

Figure 3: Cell size of detonation propagating in a H_2-NO_2/N_2O_4 mixture with $\Phi = 1.2$.

To gain further insights into the dynamics of the double cellular structure, we have studied the evolution of the shock front velocity along the centerline of the large and small cells for the $\Phi = 1.2$ case. Figures 4 a) and b) show the results obtained for the large and small cells, respectively. Whereas the velocity along the large cells decreases from 1.1 to 0.9 D_{CJ}, the velocity along the small cells exhibits larger variations in the range 1.5-0.8 D_{CJ}. This latter feature appears to be independent of the position within the large cell. The two different evolutions of the shock front velocity within the large and small cells are consistent with the different reduced activation energies associated with the two successive steps of heat release.



a) Large cell

b) Small cell

Figure 4: Variation of shock velocity along the cell centerline for detonation propagating in a H_2-NO_2/N_2O_4 mixtures with $\Phi = 1.2$ and 1.5.

5 Conclusion

In the present study, we performed numerical simulations of detonation propagating in H_2-NO_2/N_2O_4 mixtures with different equivalence ratios. All the simulations were performed with multi-step chemistry. For mixtures with $\Phi \leq 1$, a single cellular structure was observed, whereas for $\Phi \geq 1.2$, a double cellular structure was obtained, consistent with the experimental observations. In general, reasonable agreement was observed between the cell sizes measured experimentally, and predicted by the simulations. The velocity within the large cells varies between 1.1 and 0.9 D_{CJ}, while the velocity along the small cells ranges from 1.5 to 0.8 D_{CJ}. Such a difference of dynamics was attributed to the different reduced activation energies for the two exothermic steps. Future work will focus on performing statistical analysis of the detonation structure.

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