Detonation Initiation by a Temperature Gradient for a Detailed Chemical Reaction Models

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1 Introduction

In 1970 Zel'dovich et al. [1] have shown that the prescribed nonuniform temperature distributions may initiate a detonation. The idea was that a reaction wave can spontaneously ignite at the location of the minimum induction time and propagate through a combustible mixture if there is a spatial gradient in chemical induction time. The spontaneous reactive wave propagating in the direction of the gradient of reactivity and the compression wave generated by the exothermic reaction can couple and evolve into a self-sustained detonation wave, or produce a flame and a decoupled shock, depending on the gradient steepness. This mechanism, which is based on a proper synchronization of the shock wave and the exothermic reaction energy release, has since been studied extensively using 1D model (see [2] and references within for a recent review). Most of the previous works have considered a simple chemical model in which the reaction proceeds via a one-step exothermic reaction with Arrhenius kinetics. However, a one-step reaction model cannot reproduce the main properties of the combustion such as the induction time in chain-branching kinetics and detonation initiation. Development and use of the reliable detailed chemical kinetic models for fuels remains among the major challenges in combustion science, which is important for correct understanding of the combustion phenomena. It was first pointed by Sharpe and Short [3] who employed a two-step chemical model, which mimics the main features of chain-branching chemistry, that it has a profound effect on the validity of Zel'dovich's spontaneous wave concept. The evolution to detonation from temperature nonuniformities may be qualitatively different for one-step kinetics models than for chain-branching kinetic models and the evolution may be very different in different fuels (e.g., hydrogen-oxygen or methane-air) for the same initial conditions. It is therefore important to investigate the qualitative and quantitative differences in the ignition process from a temperature gradient between detailed chemical kinetics and the predictions from one-step models.

2 Induction times

The evolution from a linear temperature gradient to a detonation is investigated using high resolution numerical simulations for combustible materials whose chemistry is governed by a detailed chemical kinetics model. We employ a model which has been widely studied representing an initial linear

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temperature gradient in the fuel. Emphasis is on comparing and contrasting the results with previous studies that used simple one-step kinetics.

The burning chemistry in fuels such as hydrogen-oxygen, hydrogen-air and methane-air is governed by kinetics with chain initiation and branching reactions corresponding to Arrhenius kinetics with small if any energy release, and followed by the exothermic chain termination reactions. Both stages have well-defined times of induction zones followed by exothermic reaction zones. Figure 1 shows the induction times versus temperature calculated using different detailed chemical schemes (curves 1-6) [4] for hydrogen-oxygen mixture (left) and for hydrogen-air (right) at 1 atm; curves 7 in figure 1 are for a one-step Arrhenius kinetics. Figure 2 shows the induction times versus temperature calculated using a detailed chemical reaction model and a one-step model for hydrogen-oxygen mixture (left) and hydrogen-air (right) at different initial pressures 1, 0.1 and 0.01 atm, where curves with circles show the induction times calculated for one-step model.



Figure 1. Ignition time vs. temperature in hydrogen/oxygen (left) and in hydrogen-air (right) at 1 atm.



Figure 2. Ignition time vs. temperature in hydrogen/oxygen (left) and hydrogen-air mixtures (right) at different pressures P=1, 0.1 and 0.01 atm.

The ratio of the time scale of the induction zone to that of the exothermic reaction zone depends on the initial conditions. In hydrogen-oxygen at high pressures (higher 0.1 atm) the exothermic reaction zone is much longer than the induction zone at high temperatures (T>1200K), but at low pressures (0.01 atm) the induction reaction times are much longer than the exothermic reaction time. A one-step Arrhenius model cannot reproduce the features of chain-branching kinetics, because, in order to have a correct induction time for one-step chemistry, the activation energy must be very high, but then the thickness of the reaction zone in the flame front becomes exponentially thin. Figure 3 shows the times of induction and termination reactions at different pressures calculated using a detailed chemical kinetics scheme for hydrogen-oxygen mixture.



Figure 3. Ignition time for hydrogen-oxygen for chain branching (formation of the radicals) and chain termination (radical recombination) reactions for different temperatures and pressures 1 and 0.01 atm.

3 The Numerical Model and Results

The evolution from a linear temperature gradient to a detonation is investigated for highly reactive mixtures H_2 - O_2 and H_2 -air and for slow reactive mixture of methane-air. The governing equations are the one-dimensional time-dependent, reactive Navier-Stokes equations including the effects of compressibility, molecular diffusion, thermal conduction, viscosity and chemical kinetics for the reactive species H₂, O₂, H, O, OH, H₂O, H₂O₂, and HO₂ with subsequent chain branching, production of radicals and energy release. The equations of state for the fresh mixture, the reactive species and for combustion products were taken with the temperature dependence of the specific heats, heat capacities and enthalpies of each species borrowed from the JANAF tables. The viscosity and thermal conductivity coefficients of the mixture were calculated using the Lennard-Jones potential. Coefficients of the heat conduction of i-th species $\kappa_i = \mu_i c_{pi} / Pr$ are expressed via the kinematic viscosity μ_i and the Prandtl number, Pr = 0.75 [4, 5]. The reaction scheme for a stoichiometric H₂-O₂ mixture used in the simulations has been tested in different applications and proved to be adequate to complete chemical kinetics scheme. Computed with this chemical scheme thermodynamic, chemical, and material parameters are in a good agreement with the flame, shocks and detonation wave characteristics measured experimentally. The computational method was described in [4, 5]. It has been tested extensively to resolve the structure of the flame front with the meshes up to 64 computational cells per flame width [6].

We consider uniform initial conditions apart from a linear temperature gradient. The initial conditions at t = 0 prior to ignition are constant pressure and zero velocity of the unburned mixture. The temperature is assumed to be maximum (T₀=3000K) at x = 0 to ignite the mixture and it

decreases in the positive x-direction: $T = T_0(1 - \alpha x)$. The temperature non-uniformity is large enough for a detonation to ignite or fail inside the gradient area, so we are not concerned by the conditions outside it. The boundary condition at x = 0 is a reflective boundary condition so that this boundary is a solid, reflecting wall.

Example of the simulation for hydrogen-oxygen mixture at initial pressure 1 atm contrasting evolution of spontaneous wave for a one-step reaction and for a detailed chemical kinetics is shown in figure 4 which represents the steepest temperature gradients for successful detonation initiation. For a one-step reaction there is a heat release at the induction stage which switches on gasdynamics from the very beginning along the whole gradient, and if the gradient is sufficiently shallow the supersonic spontaneous wave followed by thermal wave decelerates, couples with the pressure wave and transforms into detonation. In the detailed chemical model if the temperature gradient is sufficiently shallow so that the reaction initially propagates supersonically, there are still no gasdynamic perturbations at the induction stage since the initiating reactions proceed with a small if any heat release and the wave of exothermal reaction follows the spontaneous wave path with the delay determined by the time scale of termination reactions. The result is that even when the thermal runaway point propagates supersonically (it does so through an evolving induction region) the thermal runaway path may differ considerably from the spontaneous wave path. The steepest temperature gradient for which a detonation can be successfully ignited depends on the heat release rate of the exothermic reaction stage compare with the rate of the induction stage and may differ considerably from the one-step model predictions (see Figs. 2 and 3). The slower the heat release rate compared to the initial induction reactions, the shallower the gradient has to be for successful ignition. It is seen from figure 4 that for initial pressure 1 atm the steepest temperature gradient for which a detonation can be ignited in H_2 - O_2 is at least one order of magnitude shallower compared to that predicted from a one-step model (left). One can see that the deceleration of the spontaneous wave and its coupling with the pressure wave takes place along the gradient region where exothermal time scale is higher than the induction one (see Figure 3). For a steeper gradient this coupling will fail in the region where the induction stage is considerably smaller than the exothermal stage and the resulting will be a deflagration wave instead of transition to detonation. In cases of lower initial pressures the steepest temperature gradient for which a detonation can be ignited is considerably shallower and it is much shallower than the gradient predicted from a one-step model.



Figure 4. Left: detonation initiation by the temperature gradient 4cm length (margin length, if the length is smaller and the corresponding gradient is steeper than there are no detonation formation) for a one-step Arrhenius kinetics. Process is represented evolution of pressure (solid lines) and temperature (dashed lines) profiles, time intervals are $1\mu s$. Right: detonation initiation by the steepest

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temperature gradient of 50cm length for a detailed chemical kinetics model. Process is represented with pressure (solid lines) and temperature (dashed lines) profiles, time intervals are 4μ s.

4 Slow reactive mixtures (methane-air)

The evolution from a linear temperature gradient to a detonation is investigated also for slow reacting methane-air mixtures at different initial pressures, using a reduced detailed chemical scheme [7], which captures the main properties of methane-air chain-branching reactions. Induction times versus temperature for methane-air mixtures at different initial pressures, calculated using the chemical scheme [7] are plotted in figure 5. Compared to the case of highly reactive (H_2 -O₂ and H_2 -air) mixtures the ignition times for methane-air calculated using a detailed chemical model differ much stronger from that calculated with a one-step model. Accordingly, it is expected that the steepest temperature gradient for which a detonation can be ignited in methane-air mixtures will be much shallower compare to that predicted from a one-step model. Indeed, the simulations show that for a detonation can be successfully ignited is profoundly shallower than in the case of hydrogen-air mixtures at the same pressures and considerably differs from the predictions from a one-step model.



Figure 5. Induction time vs. temperature in methane-air mixtures at different pressures compared to the induction times given by a one-step Arrhenius model (curves with circles).

5 Conclusions

The analysis shows that there is substantial difference in the dynamics of the detonation initiation by a temperature gradient for a detailed chemical model and for a simplified one-step chemical model. Identification of the realistic kinetic pathways and accurate kinetic–transport models are essential for the understanding of reliable conditions of a detonation initiation by the temperature gradient. As an example, the detailed chemical kinetics for H2/O2, H2/air and methane-air were considered. The results of the presented numerical simulations show that detailed chain branching kinetic models have a profound effect on the validity of the spontaneous wave propagating through gradients of temperature. It is shown that the evolution to detonation from the temperature nonuniformities is is profoundly different for detailed chain branching kinetic models than for one-step kinetic models and that the evolution is different fuels, such as hydrogen-air or hydrocarbon-air. The steepest

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temperature gradient capable to initiate detonation is at least one order of magnitude shallower compared to that predicted from a one-step model for a highly reactive mixture (H2/O2), and the difference even more significant for slow reactive mixtures (methane/air). The obtained results make questionable applicability of the gradient mechanism as a mechanism of the transition from deflagration to detonation. In a real system, the temperature gradients, which may appear in the form of hot spots and the like, are likely not satisfy the criteria necessary to initiate detonation. The usage a simplified one-step model must be considered with greatest discretion and requires at least a very careful analysis of the correctness of its application and interpretation.

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