

Regimes of Chemical Reaction Waves Initiated by Initial Temperature Gradient: Detailed Chemical Reaction Models

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1 Introduction

The ignition of the chemical reaction is one of the most fundamental problems in combustion physics. One needs to know how combustion starts and how initial conditions affect initiation of reaction wave which propagates out from the ignition location. What type of combustion wave can be formed depending on the ignition conditions? In most practical cases ignition arises from a small area of combustible mixture which is locally heated by means of electric spark, hot wire, focused laser light and the like. Such a local energy release results in the formation of the initial non-uniform distribution of temperature, pressure, concentration etc., which determines further evolution of the reaction wave depending on the mixture reactivity and the initial environmental conditions. For the first time possible regimes of propagating chemical reaction wave initiated by the initial temperature non-uniformity (gradient) have been studied by Ya. B. Zeldovich [1]. The concepts of the spontaneous reaction wave, introduced by Zeldovich [1] opened an avenue for studying scenario of the ignition of different regimes of combustion wave initiated by the initial non-uniformity and therefore of great fundamental and practical importance. This matter has been subject of many subsequent studies, majority of which has employed a one-step Arrhenius reaction model similar to [1]. Two-step and three-step models were also used to model chain-branching kinetics and to study the initiation of detonation [2-5]. In particular the role of chain-branching cross-over temperature in shock-induced ignition was studied by numerical simulation [5]. It was shown that the one-step model is not appropriate for simulating detonation initiation in systems governed by chain-branching explosions [6]. These studies have shown that there is essential difference between the results obtained using two-step or three-step models and that obtained using a one-step model. All the same the quantitative difference between a one-step model and detailed chemical model important for practice remained unclear. It is known that, for example, the ignition energy for methane-air computed with one-step model differs by two orders of magnitude from the experimentally measured value [7]. Besides, all the

previous studies have been solely focused on a special case of a detonation ignition from initial temperature gradient, while the problem in question is much wider being associated with the ignition of different combustion regimes. It is clear that the models with fairly simplified chemical kinetics and gas-dynamics though often allow analytical analysis and reduce computational cost, but can describe only a few major qualitative properties of the phenomena if any, and with some quite poor accuracy. To understand quantitative effects one should use full gas-dynamics with real transport and thermodynamic properties for multi-component gaseous mixtures and detailed chemical kinetics models. Such a level of modeling is especially important when studying unsteady processes, such as the ignition.

2 Problem Setup

This paper dedicated to study combustion regimes initiated by the initial temperature gradient using high resolution numerical simulations for a multispecies transport model and detailed chemical kinetic schemes for combustible gaseous stoichiometric mixtures H_2-O_2 and H_2 -air whose chemistry is governed by chain-branching kinetics. The initial conditions are assumed uniform apart from a linear temperature gradient. Prior to ignition at $t=0$, pressure is constant and velocity of the unburned mixture is zero. At the left boundary at $x=0$ the conditions are for a solid reflecting wall and the initial temperature $T=T^*$.

$$T(x,0) = T^* - (T^* - T_0)(x/L), \quad 0 \leq x \leq L, \quad (1)$$

$$P(x,0) = P_0, \quad u(x,0) = 0. \quad (2)$$

The initial temperature gradient is characterized by the temperature difference between the top left edge $T(0,0)=T^*$ and the temperature outside the gradient $T(x>L,0)=T_0$ and by the gradient steepness $(T^*-T_0)/L$. The “gradient scale” L characterizes the gradient steepness for fixed value of (T^*-T_0) and can be viewed as the size of the area where the initial temperature gradient was created by the energy input or the like.

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 reacting species (H_2O , H_2 , H , O_2 , O , OH , HO_2 , H_2O_2) with subsequent chain branching, production of radicals and energy release. Numerical method used in the simulations, kinetic model and the full set of equations were presented in [8, 9]. Thorough convergence and resolution tests have shown that the resolution of 50 computational cells over the width of laminar flame ($\Delta = 0.0064\text{mm}$ at $P_0 = 1\text{atm}$) was enough for the convergence and to ensure that the resolution is adequate to describe and to capture details of the problem in question and to avoid computational artifacts. The appropriate computational cell size at higher pressure is smaller proportionally to the pressure. Sensitivity analysis for this chemical scheme as well the computed thermodynamic, chemical, and material parameters for the used chemical scheme have shown an excellent agreement with the experimentally measured flame, shock waves and detonation wave characteristics [8, 9].

3 Regimes of chemical reaction wave initiated by the temperature gradient in H_2-O_2

The evolution of the reaction wave velocity (solid line) and the pressure wave velocity (dash-dotted line) for the gradient with the scale $L=8\text{cm}$ in H_2/O_2 gaseous mixture at the initial pressure 1atm , $T^*=1500\text{K}$, $T_0=300\text{K}$ is shown in Fig.1 (left). The velocity of the spontaneous wave was determined from the trajectory of the maximum H-radical iso-line. The velocity of the pressure wave was determined from the trajectory of the maximum pressure point of the pressure-wave profile. It is seen that the velocity of spontaneous wave decreases while it propagates along the gradient, and reaches the minimum value at the point close to the cross-over temperature where it is caught-up with the pressure

wave which was generated behind the high-speed spontaneous wave front (indicated by dashed vertical line). After the intersection of the spontaneous wave front and the pressure wave, the spontaneous wave transforms into combustion wave and the pressure wave steepens into the shock wave. For a shallower gradient, such that the minimum speed of spontaneous wave is of the order of the sound speed $a_* = a(T^*)$ at the top of the gradient, the intensity of the shock wave formed ahead of the reaction wave is sufficient to accelerate the reaction in the flow formed behind the shock. As a result, the pressure peak is formed at the reaction front, which grows at the expense of energy released in the reaction. After the pressure peak becomes large enough, it steepens into a shock wave, forming an overdriven detonation wave (the peak of the maximum velocity U_{sp} at the point $x/L=0.65$ in Fig. 1 (left)). The corresponding evolution of the temperature and pressure profiles is shown in Fig. 1 (right). For a steeper temperature gradient (e.g. $L = 7\text{cm}$) the velocity of spontaneous wave in the minimum point, where the pressure wave overtakes the reaction wave, is not sufficient to sustain synchronous amplification of the pressure pulse in the flow behind the shock. As a result, the pressure wave runs ahead of the reaction wave and the velocity of the reaction wave decreases resulting in deflagration.

Possible combustion regimes obtained from the numerical studies with the detailed chemical kinetics depending on the gradient steepness and the speed of spontaneous wave relative to the characteristic velocities of the problem are shown in Fig. 2, which represents diagram for U_{sp} in the minimum point versus the inverse gradient steepness (L). The pressure waves generated during the exothermic stage of reaction can couple and evolve into a self-sustained detonation wave, or produce a flame and a decoupled shock depending on the gradient steepness. The outcome depends on the gradient steepness and the ratio between the speed of spontaneous wave at the point where its velocity reaches minimum (minimum point) and the characteristic velocities U_f , $a_0 = a(T_0)$, $a^* = a(T^*)$, a_N , a_{CJ} , U_{CJ} . Here U_f is normal laminar flame speed; a_0 , a^* , a_N , a_{CJ} are the sound speeds at the points $T = T_0$ and $T = T^*$, at the Newman point and at the Chapman-Jouguet point. U_{CJ} is the velocity of the Chapman-Jouguet detonation. In summary, there are the following modes of reaction waves initiated by the initial temperature gradient. For $U_{sp} < U_f \ll a_s$ (domain 0), the rate of the heat transfer by thermal conduction is greater than the spontaneous wave velocity, and the resulting regime is a deflagration wave propagating due to the thermal conduction with the normal flame velocity $U_f = 10\text{m/s}$. Ignition of the deflagration is bounded from below by the minimum size of the hot region, for which the rate of heat removal from the "hot wall" is higher than the normal flame velocity. Domain (0) in Fig. 2 corresponds to the regime (4) in the Zeldovich's classification [1]. If the spontaneous wave velocity in the minimum point is greater than the normal flame speed but less than the sound speed in the unperturbed media $U_f < U_{sp} < a_0$ (domain 1) then the "fast" deflagration is formed, which is an "intermediate asymptotic" [10]. The pressure wave overtakes the deflagration wave, and the fast deflagration wave propagates at nearly constant pressure. If $a_0 < U_{sp} < a^*$, then pressure wave overtakes the reaction wave to form a weak shock wave that compresses and heats the gas further speeding up the deflagration wave (domain 2). There are two different scenarios for the domain 3, where $a^* < \min\{U_{sp}\} < a_{CJ}$. If $a^* < \min\{U_{sp}\} < a_N < a_{CJ}$ the reaction wave accelerates behind the shock and the transition to detonation occurs due to the formation and amplification of the pressure peak at the front of the reaction wave. If $a_N < \min\{U_{sp}\} < a_{CJ}$ then a quasi-stationary structure consisting of a shock wave and reaction zone is formed, which transforms into a detonation propagating down the temperature gradient. In both cases the spontaneous reaction wave is accelerated in the flow behind the shock wave and transitions to a detonation wave. Both of these regimes correspond to more detailed classification of the regime (3) in the classification of [1]. If $a_{CJ} < \min\{U_{sp}\}$ (domain 4), then the

intersection of the pressure wave and the spontaneous reaction wave creates a classical structure of a detonation wave with the leading shock wave initiating the reaction. Finally, the limiting case of a very shallow temperature gradient $\nabla T \rightarrow 0$, $U_{sp} \rightarrow \infty$ corresponds to the adiabatic explosion. All the described regimes provide more detailed classification of possible propagating combustion regimes disclosed first by Zeldovich [1] for a one-step chemical model. Figure 3(left) shows the limiting inverse gradient steepness (L) corresponding to the boundaries between domains 1, 2, 3, 4 in Fig. 2 versus temperature T^* at the top of the gradient calculated for stoichiometric hydrogen-oxygen mixture using the detailed chemical model. Similar diagram for the boundaries between domains of the different modes but calculated using the one-step chemical model, is shown in Fig. 3(right). One can see that at the initial pressure of 1atm actual steepness of the temperature gradient initiating any modes of the combustion wave is much less steeper than that predicted by a one-step chemical model. The size of the initial inhomogeneity essential for initiation of any possible regime of combustion is by at least one-two orders of magnitude larger than that predicted by a one-step chemical model.

4 The Pressure Dependence

The temperature dependence of the induction time changes when the initial pressure is changed. At lower pressures, the induction zone is much longer than the chain termination exothermic zone. At high pressures they become of the same order. The cross-over temperature at which the equilibrium of the induction and termination stages take place is known as “the extended second explosion limit” [11]. At higher pressures this limit shifts to higher temperatures and correspondingly at lower pressures it shifts to lower temperatures. Therefore, the initiation process at low pressures is qualitatively similar to the initiation of combustion waves at normal pressure for high temperature T^* . In this case steepness of the temperature gradient required to implement the regimes with the shock and detonation waves decreases rapidly, and the “speed” limits separating regions of different modes are determined by the sound speeds a_0 , a^* and a_{CJ} . On the contrary, for high-pressure the scenario is somewhat more similar to that realized for a one-step model or for low values of T^* at the point $x = 0$, resulting in a decrease in the limits of ranges for the realization of the regimes 2 and 3. At the same time since at the high pressure induction time is considerably smaller at low temperatures, the minimal steepness of the gradients necessary for the implementation of all the regimes and in particular for the direct initiation of detonation is significantly increased (minimal L decreases). The scales of the gradient for different initial pressure calculated for $T^* = 1500\text{K}$ and $T_0 = 300\text{K}$ are shown in Fig. 4. At pressures above 10atm the time of induction phase exceeds the time of the exothermic reactions. Therefore, all combustion regimes formed at the high-pressure are similar to the scenario at low T^* , which is defined by the speed of spontaneous wave at $x = 0$. At sufficiently high pressures (of the order 50atm) direct initiation of detonation by the temperature gradient in the hot spot of size of about 3-5mm becomes possible [12].

5 Conclusions

Because of the difference in the induction time and the time when the exothermic reaction starts the steepness of the temperature gradient required for initiation combustion regimes differ considerably for a one-step and detailed chemical models for the identical initial conditions. The difference between a one-step model and a detailed chemical model is especially noticeable at low pressures and for slow reacting mixtures. For example, the steepness of temperature gradient for the direct initiation detonation in hydrogen-air mixture is about hundred times less than it is predicted by a one-step model, see figure 4 (right). The obtained results answer the question: what are the scales of the energy deposition which capable to ignite one or another regime of the combustion wave, which is important for practical applications, for *risk assessment*, for safety guidelines in industry and nuclear power plants, and to minimize “accidental” explosions.

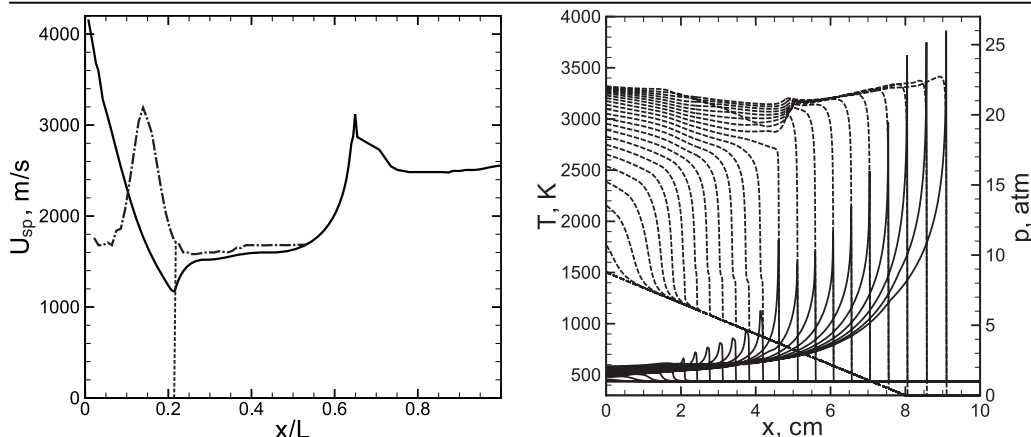


Figure 1 (left). Velocities of the spontaneous wave (solid lines) and pressure wave (dash-dotted lines) computed for the temperature gradient $L=8\text{cm}$, $T^*=1500\text{K}$ in $\text{H}_2\text{-O}_2$ mixture.

Figure 1 (right). Evolution of the temperature (dashed lines) and pressure (solid lines) profiles during the formation of the detonation in Fig. 1 shown at intervals $2\mu\text{s}$.

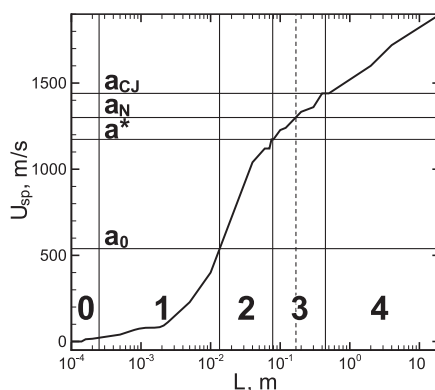


Figure 2. Regimes of the reaction wave propagation initiated by temperature gradients of different scales in $\text{H}_2\text{-O}_2$ mixture, $P_0=1\text{atm}$.

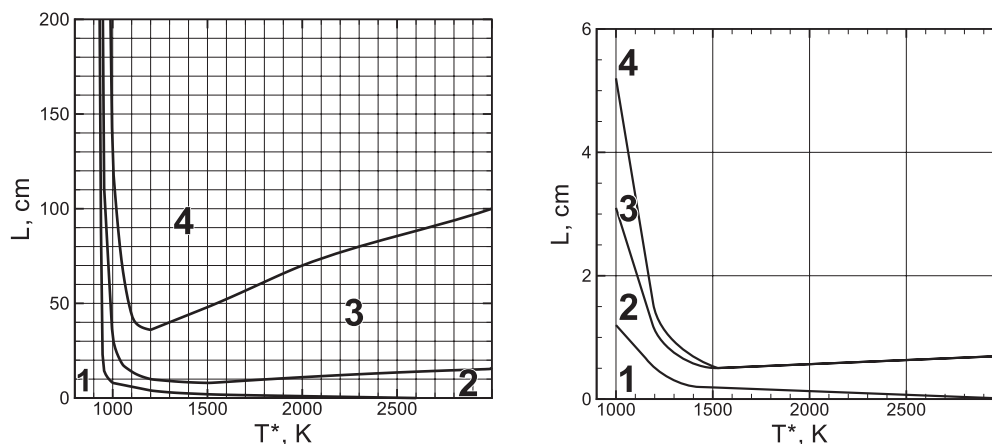


Figure 3. Left: Scales (inverse steepness) of the temperature gradient corresponding to the boundaries between regimes 1, 2, 3, 4 in Fig. 3 calculated for a detailed chemical model; Right: the same but calculated for a one-step chemical model.

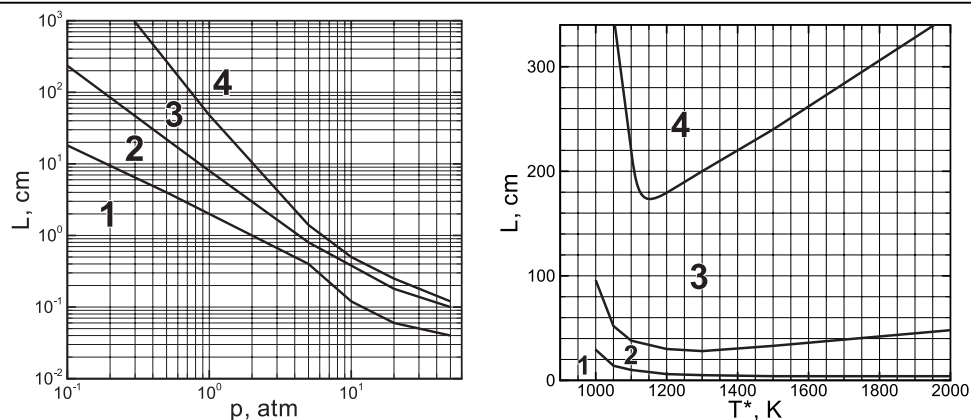


Figure 4. Left: Scales of the temperature gradient required for initiation of the regimes 1, 2, 3, 4 depending on the initial pressure of H_2 - O_2 mixture ($T^*=1500K$, $T_0=300K$). Right: scales of the temperature gradient in H_2 -air mixture required for initiation of the regimes 1, 2, 3, 4 depending on T^* value; $T_0=300K$, $P_0=1atm$.

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