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A Microscopic Analysis of Premixed Hydrogen-Oxygen Auto-ignition

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Abstract. Combustion is a complex problem involving multi-stage chemical reactions and multi-scale physics. The microscopic process of chemical reactions has obvious stochastic character and may bring important influence to combustion phenomena both locally and globally. In this study, we employ a stochastic simulation algorithm (SSA) to simulate the microscopic hydrogen-oxygen auto-ignition process. Statistical result of SSA calculation shows that fluctuation is controlled by both temperature and microscopic volume. The non-homogeneous distribution of radicals caused by local fluctuation may cause the difference between average microscopic quantities and their macroscopic counterparts due to some radical-radical reactions.

INTRODUCTION

Combustion is a complex problem involving multi-stage chemical reactions and multi-scale physics. It involves not only a large amount of chemical reactions but also various physical interactions at different scales (e.g. turbulent combustion). For instance, in some complex combustion problems, such as the plasma assisted combustion, electronically excited molecules play important roles in the reaction kinetics. There is increasingly demanding to understand combustion with more details.

Studies of combustion are usually in the continuum frame for both reaction kinetics and fluid applications. Chemical reaction behavior, however, is essentially a collection of effective collisions among reactant molecules, which means that reaction at the microscopic scale has a discrete and stochastic nature. In fact, Frisque et al. [1] showed the fluctuation of ignition delay time for methane auto-ignition using a stochastic simulation algorithm (SSA). Kinetic simulation of chemical reactions has also been done using the direct simulation Monte Carlo (DSMC) method. For instance, Bird [2] demonstrated the feasibility of DSMC to study the auto-ignition process of hydrogen-oxygen mixture.

In this paper, we analyze the microscopic features of auto-ignition of gas mixture, and will focus on the stochastic character of auto-ignition of hydrogen-oxygen mixture.

MICROSCOPIC PROCESS OF CHEMICAL REACTIONS

Combustion involves a large set of element reactions. Each reaction speed is controlled by the reaction rate k and the concentration c_i of related reactants. At the microscopic level, the reaction speed is determined by the collision frequency of molecules and reaction probability for a collision having reaction. Namely, only some collisions will have possibility to cause reactions when the collision energy (E_c) is larger than reaction threshold energy (E_0). The reaction probability P_{reac} is called steric factor.

The steric factor of collisions with E_c can be derived from *ab initio* calculations or reaction models. When P_{reac} is known, we can sum up all possible effective collisions to get a macroscopic overall reaction rate k as follows,

$$k = v \int_{\frac{E_0}{kT}}^{\infty} P_{\text{reac}} \cdot f\left(\frac{E_{tr}}{kT}\right) d\frac{E_{tr}}{kT}, \quad P_{\text{reac}} = \frac{\sigma_r}{\sigma_T}. \quad (1)$$

The detailed expression for k can be derived for specific models. For the widely used TCE model [3] in DSMC simulations, P_{reac} is assumed as a function of the total collision energy. The reaction rate can be expressed as the Arrhenius form after the integration over the collision energy.

$$P_{\text{reac}} = C_1 (E_c - E_0)^{C_2} (1 - E_0/E_c)^{\bar{\zeta} + 3/2 - \omega_{AB}}, \quad (2)$$

$$k(T) = \frac{2C_1 \sigma_{\text{ref}}}{\pi^{0.5} \varepsilon} \left(\frac{2kT_{\text{ref}}}{m_r} \right)^{0.5} \frac{\Gamma(\bar{\zeta} + C_2 + 5/2 - \omega_{AB})}{\Gamma(\bar{\zeta} + 5/2 - \omega_{AB})} \frac{k^{C_2}}{T_{\text{ref}}^{1-\omega_{AB}}} T^{C_2 + 1 - \omega_{AB}} \exp\left(-\frac{E_0}{kT}\right). \quad (3)$$

For most reactions, the average reaction probability is far less than 1. This reveals the fact that a single reaction event has stochastic nature. For a given system and a specific reaction type, the next time for a reaction event, t_r , is a random variable with its average value of t_0 . The distribution function of t_r is in the exponential form and t_0 is determined by the reaction rate.

$$f\left(\frac{t_r}{t_0}\right) = e^{-\frac{t_r}{t_0}}, \quad t_0 = \frac{1}{Vkn_A n_B}. \quad (4)$$

The time for collisions to have N reaction events is expressed as $t_{r,N}$ and its distribution function is Poisson distribution f_N . Figure 1 shows the distribution of f_N with an average value of Nt_0 .

$$f_N\left(\frac{t}{t_0}\right) = e^{-t/t_0} \cdot \frac{(t/t_0)^{N-1}}{(N-1)!}, \quad t_0 = \frac{1}{Vkn_A n_B}. \quad (5)$$

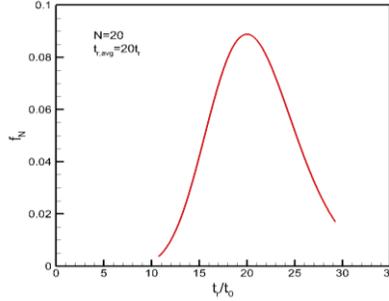


FIGURE 1. The distribution of f_N when N is 20.

The stochastic character of reactions is important from the microscopic viewpoint. First, reaction events are stochastic behaviors, which will cause fluctuations in species concentration in the space over the time. It means that the concentration distribution in the space will not be uniform even for a well-mixed system. Particularly, at the initial stage of a combustion setup, new species such as radical species will be accumulated at a relatively slow pace. Then the species concentration can only be changed in a discrete manner. Second, molecules will move around due to their thermal motion, then species concentration will not keep constant even when reactions are frozen. Therefore, fluctuation is normal for combustion at the microscopic level. We will also show that stochastic character can lead to certain macroscopic effect for some combustion problems as the statistical behavior will depart from the classical chemical kinetic results.

ANALYSIS OF AUTO-IGNITION OF HYDROGEN-OXYGEN MIXTURE

Combustion is a field that involves many subjects including reaction kinetics, fluid mechanics and heat transfer. Among various combustion problems, auto-ignition is a relatively simple but important one, and hydrogen-oxygen combustion is a classical problem. Therefore, we choose the auto-ignition of H_2/O_2 mixture to analysis the microscopic mechanism of combustion.

Reaction Kinetics of Hydrogen-Oxygen Auto-Ignition

The mixture of hydrogen and oxygen will not ignite at low temperature if no energy is input. But when the initial temperature is higher than the so-called explosion limit (Fig. 2), the mixture can automatically ignite after a short time. This phenomenon is known as auto-ignition and the time to ignite is defined as ignition delay time.

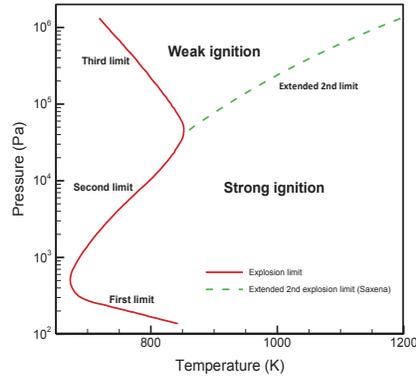


FIGURE 2. Explosion limits of hydrogen-oxygen mixture [4] where the dashed line is the extended second explosion limit calculated using the reaction mechanism of [5].

The auto-ignition process involves many chain reactions and radicals like H, O and OH. It usually owns a relatively long period of radical production stage before the heat releasing stage, as shown in Fig. 3. This radical growth period, known as the induction period, is controlled by a few key reactions. Thus a reduced reaction mechanism is enough to describe the reaction process at the induction period. In the present study, the following 8-reaction reduced mechanism [6,7] is adopted.

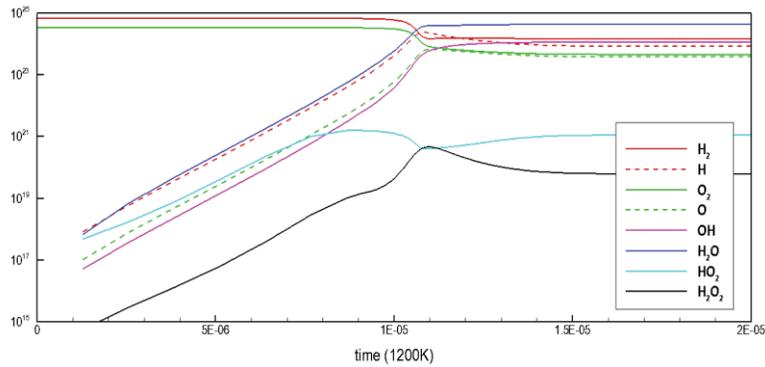
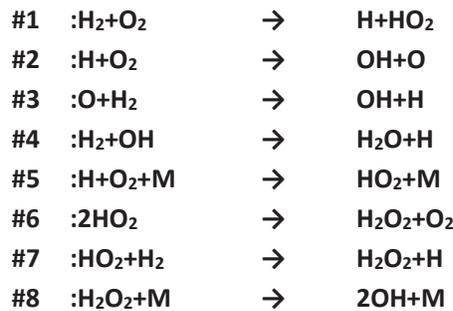


FIGURE 3. The time history of species concentration in an auto-ignition process when $T=1200\text{ K}$, $n=10^{25}\text{ m}^3$, 67% H_2 +33% O_2 .



For each element reaction, the reaction rate depends on the activation energy E_a and reaction order so it is determined by the system temperature and reactant concentrations (or, for given composition, the pressure). For the above 8-reaction mechanism, it has a 3-step chain reaction path (#2~#4) that is important for all conditions, and an extra low-temperature reaction path (#5~#8) that is only important at the low temperature and high pressure range. The two paths are shown in Fig. 4.

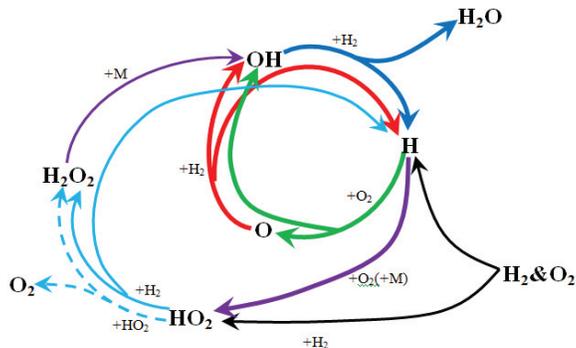


FIGURE 4. The reaction path of hydrogen-oxygen ignition during the induction period.

In general, the first few radicals (H) in a H_2/O_2 mixture are produced from the initial reaction #1. As radicals gradually accumulate, the 3-step chain reactions #2~#4 become the most important radical production path, which makes the radical production speed keep accelerating until the final explosion moment. But as the temperature decreases, reaction #5 will become an important reaction for H consumption, which competes with reaction #2. Reaction #5 consumes H as a termination reaction that slows down the H production speed of #2~#4. Thus the ignition delay time will increase dramatically. The state when H consumption rate by #5 is identical to H production rate by #2~#4 is defined as the extended second explosion limit, and the limiting density can be derived as $n_M = 2k_2/k_5$ because the product rate is dominated by the reaction rate of #2. When the temperature is lower than this limit, the low temperature reaction path #6~#8 will overtake the high temperature path #2~#4. Specifically, in low temperature auto-ignition (also called weak ignition), most H is converted into HO_2 , and then HO_2 participates in reaction #6 and #7 to produce more radicals like H and H_2O_2 . As a result of the path change, the low temperature ignition time will increase greatly than that of high temperature as shown in Fig. 5.

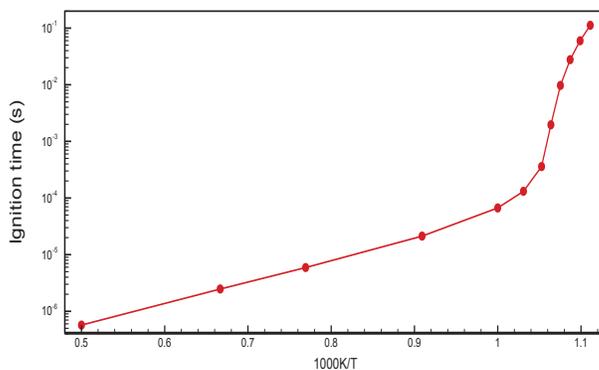


FIGURE 5. Ignition delay time of H_2/O_2 mixture at temperature range 900~2000 K, 67% H_2 +33% O_2 , $n=10^{25} m^{-3}$. Ignition criterion is taken as the inflection point of OH concentration.

For a homogeneous mixture, auto-ignition is often assumed as a zero-dimensional problem. This assumption is reasonable for high-temperature auto-ignition although disturbances exist in real experimental environment. However for low temperature auto-ignition, the ignition delay time is much longer and disturbances will exert stronger influence on the ignition process. As a result, the ignition process will show several non-ideal characters [8], such as the non-homogeneous ignition process, data scatter of ignition delay time derived from experiments, and ignition time discrepancy between reaction kinetic calculations and experimental results. In addition to the macroscopic disturbances, like pressure fluctuation and residual radical impurities, microscopic fluctuation of radical production may be another critical reason.

Stochastic character of auto-ignition at microscopic scale

Molecules have discrete character at the microscopic scale and species concentration cannot be infinitesimal. The time for a reaction to produce one radical usually depends on the spatial volume under consideration. For instance, the average time (t_1) to produce the first H through reaction #1 is inversely proportional to volume V as shown in (6).

$$t_1 = \frac{1}{Vk_1 n_{H_2} n_{O_2}}. \quad (6)$$

As collisions are stochastic, the reaction process varies case by case. Figure 6 shows the ignition delay time for a H_2 - O_2 mixture predicted using the DSMC method. The simulated number of molecules represents the concerned volume as one simulated particle here corresponds to one real molecule. Clearly, the results depend on the volume and are stochastic. The difference, however, decreases when the volume increases.

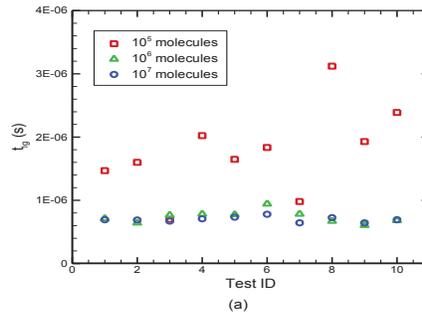


FIGURE 6. Ignition delay time predicted using DSMC with different number of molecules. (67% H_2 +33% O_2 , $p = 1\text{atm}$, $T = 1500\text{K}$).

The ignition delay time is a stochastic variable, and its distribution can be derived using statistics with a large amount of tests. The numerical cost of DSMC simulation, however, is big for doing so, and we choose the stochastic simulation algorithm (SSA) to get the distribution information. SSA [9] doesn't deal with the microscopic collisions among molecules, but considers only the stochastic process of each chemical reaction. In SSA simulation, a random time is generated for each single reaction following the distribution function described by equation 6, and the combustion process is advanced by adding the reaction events. Frisque [1] used this method to study the auto-ignition of methane, and found that the microscopic ignition process has obvious fluctuation, which affected by volume and temperature.

As explained, a large amount of reaction events will continuously occur from the appearance of the first radical to the final ignition. The stochasticity in these events is accumulated gradually and eventually forms the final fluctuation of ignition time. Here we use the SSA method to examine the fluctuation of different ignition stage. A specific stage is identified by its radical concentration, like H. By running the SSA calculations many times, statistical result of the auto-ignition process can be derived, such as the time distribution and its standard deviation.

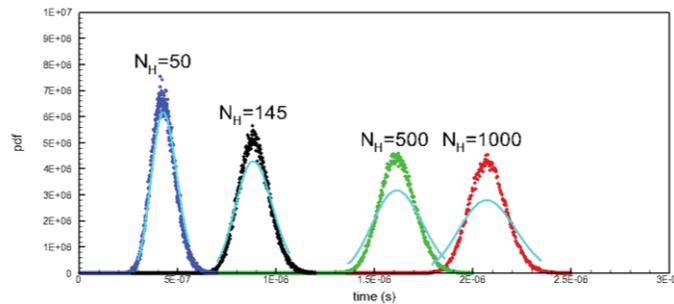


FIGURE 7. The distribution of time to reach a certain stage in a microscopic auto-ignition where the dots are from SSA calculations and the lines are based on Eq. (7). Each stage is defined with a specific H concentration. $T=1200\text{K}$, $n=10^{25}\text{m}^{-3}$, 67% H_2 +33% O_2 , $V=10^{-15}\text{m}^{-3}$.

Figure 7 shows the distribution of time to reach a specific H concentration. As can be seen, the fluctuation keeps growing in the early stage and gradually becomes steady when H concentration is high. This can be explained with the slow radical production rate in the early stage. As H concentration is rather low at early time, the radical like H is mainly produced from the initial reaction #1, which is a very slow process with strong stochastic character. When H concentration is higher, the radical production rate increases rapidly and the stochastic character is no longer significant. The standard deviation of time distribution is shown in Fig. 8, which shows that the deviation reaches a steady state when H concentration increases. It also shows that the deviation depends strongly on the mixture temperature. The lower the temperature, the larger the standard deviation of the fluctuation.

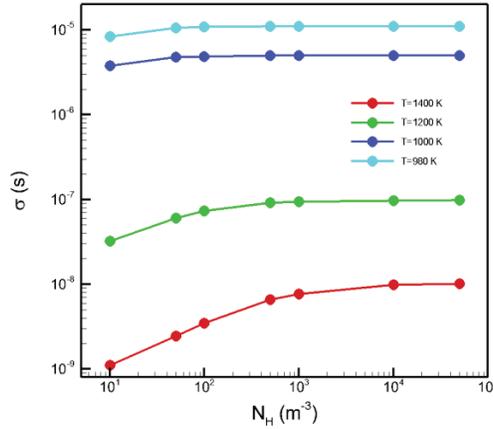


FIGURE 8. The evolution of standard deviation of time distribution during the auto-ignition process. $T=980\sim 1400$ K, $n=10^{25}$ m⁻³, 67% H_2 +33% O_2 , $V=10^{-15}$ m⁻³.

To derive an approximation expression for the standard deviation, some approximations are made. From expression (5), the standard deviation of the time distribution is $\sqrt{N}t_0$. At the early stage of the ignition, the production of radical H is linear, thus the deviation can be well represented as $\sqrt{N_H}t_0$. Noticing that variation of deviation in Fig. 7 is small with the change of N , we choose the state when H production speed through reaction #1 and reaction #2~#4 is identical. Namely $N_H = Vn_{H_2} k_1/k_2$. Then we get the expression for the standard deviation as

$$\sigma = (N_H)^{1/2} t_0 = \left(\frac{1}{k_2 n_{O_2}} \cdot \frac{1}{V k_1 n_{H_2} n_{O_2}} \right)^{0.5}. \quad (7)$$

The results from expression (7) are also potted in Fig. 7. As can be seen, the agreement between statistical results and the approximated expression is satisfactory, especially during the early stage where the product is nearly linear. From expression (7), we find that the fluctuation is affected by the volume, reaction rate of #1 and #2, the concentration of H_2 and O_2 .

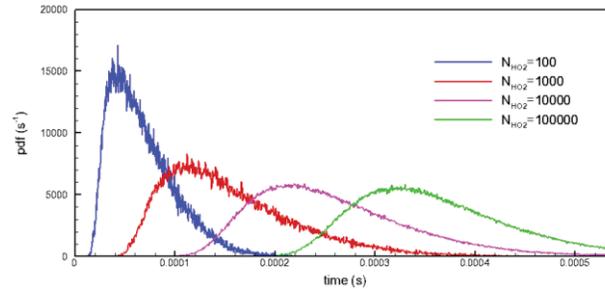


FIGURE 9. The distribution of time to reach a specific stage at a microscopic auto-ignition. Each stage is defined with a specific HO_2 concentration. $T=950$ K, $n=10^{25}$ m⁻³, 67% H_2 +33% O_2 , $V=10^{-15}$ m⁻³.

For low temperature auto-ignition, the change in reaction mechanism not only increases the ignition delay time but also intensifies the microscopic fluctuation. Radical HO₂ now has the highest concentration among all radicals due to reaction #5. So we choose HO₂ concentration to define a specific stage for low temperature analysis. Figure 9 shows the fluctuation character of auto-ignition at 950K. Noticing that ignition delay time at 950K is only 0.54 ms, the time fluctuation in Fig. 9 is rather large. The increased fluctuation is mainly from the complexity of H's reaction path. After one H is produced, it can either be consumed by reaction #2 and then produce more radicals, or consumed by reaction #5 as a termination. This fluctuation will increase when temperature decreases as shown in Fig. 10.

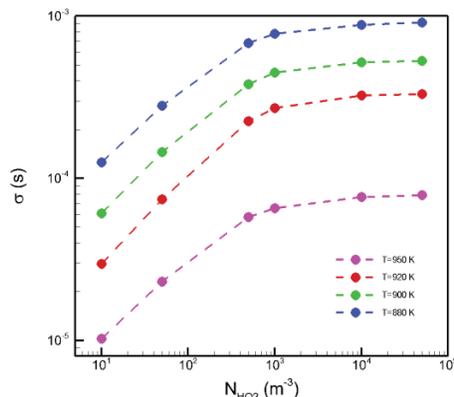


FIGURE 10. The evolution of standard derivation of time distribution during the auto-ignition process. $T=880\sim 950$ K, $n=10^{25}$ m³, 67%H₂+33%O₂, $V=10^{-15}$ m³.

The above analysis is focused on the microscopic auto-ignition and its fluctuation character. We learn that the microscopic stochastic character can also influence the overall ignition process. If we divide a macroscopic scale region into many microscopic volumes, the overall reaction rate and radical concentrations can be derived by summing up all the microscopic results when interactions between small volumes are neglected. When the reaction rate for a reaction depends nonlinearly on a concentration, the averaging of microscopic quantities will not be the same as their macroscopic counterparts. Taking reaction #6 as an example, the average reaction rate of microscopic process is higher than the macroscopic calculation as shown in expression (8). As a result, the average concentration of HO₂ is smaller than 0-D calculation using macroscopic reaction rate because more HO₂ is consumed through reaction #6. A comparison between macroscopic concentration and microscopic average is shown in Fig. 11 where two values of the microscopic volume are given. From Fig. 11, the difference is negligible at early time, but increases with the time development. It also shows that the departure from the macroscopic value increases when the

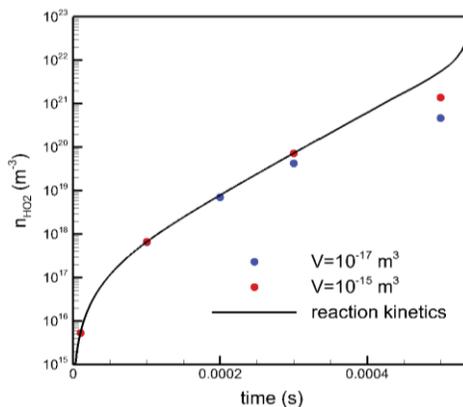


FIGURE 11. Time history of HO₂ concentration: solid line is macroscopic result, symbol is the statistical result of microscopic ignition using of SSA. $T=950$ K, $n=10^{25}$ m³, 67%H₂+33%O₂.

microscopic volume decreases. It should be mentioned that the present analysis does not consider the interaction among microscopic volumes and thermal motion of molecules is neglected. The finding here, however, is very interesting and deserves further investigation.

$$\#6: \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 : \frac{1}{N} \sum_N (k n_{\text{HO}_2} n_{\text{HO}_2}) = \frac{k}{N} \sum_N (\Delta n_{\text{HO}_2} + \bar{n}_{\text{HO}_2})^2 > k (\bar{n}_{\text{HO}_2} \bar{n}_{\text{HO}_2}). \quad (8)$$

CONCLUSION

This study has shown the stochastic character of chemical reaction and how it can affect microscopic auto-ignition process. The fluctuation of ignition at the microscopic scale is mainly due to the discrete nature of collisions and appears at the early stage where radical production process is slow. The fluctuation is more severe with smaller volume and lower temperature, which means that low temperature combustion may be more complicated. It is interesting to know that microscopic average may be different from its macroscopic counterpart due to microscopic fluctuation.

ACKNOWLEDGMENTS

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