

Influence of Microscopic Stochastic Properties on the Auto-Ignition of Hydrogen / Oxygen Mixture

Chao Yang¹, Quanhua Sun^{1,2}

¹LHD, Institute of Mechanics, Chinese Academy of Sciences

²School of Engineering Science, University of Chinese Academy of Sciences
Beijing, China

1 Introduction

Combustion has been widely studied for fundamental research and industrial applications. Recent efforts have been paid on advanced engine design and combustion phenomena exploration in extreme conditions, among many others [1]. For instance, the combustion in scramjet engine involves flow structures in the length of 1 micron where the flow is supersonic. The combustion behavior in such a small scale may not be well described using the macroscopic chemistry. There are also reports showing that the ignition delay time in shock tube cannot be explained using current kinetic models in the low temperature range. It is therefore interesting to understand the combustion behavior at the micron scale or in low temperature range.

A picture of the multi-scale processes and prediction models in combustion has been given by Gou et al. [2]. As it shows, the combustion processes at the micron scale involve molecular collisions and transports, which requires approaches using statistical mechanics and direct modeling. A brute-force effort has been made to investigate the spontaneous hydrogen-oxygen combustion using the direct simulation Monte Carlo (DSMC) method [3]. The DSMC simulation is able to mimic all the collisions and microscopic motions in a small volume, but its large numerical expense prohibits it to obtain statistical behavior of spontaneous combustion. If molecular motion is assumed to be unimportant, then the stochastic simulation algorithm (SSA) can be applied to study efficiently the stochastic behavior of the auto-ignition delay time [4]. The cost of a SSA simulation, however, increases rapidly with the number of molecules and collisions.

In this work, we continue to study the auto-ignition of premixed hydrogen/oxygen mixture at the microscopic level and will focus on the influence of the microscopic stochastic properties. We first develop an efficient stochastic simulation method so that we can study the ignition process at low temperature and relative large volume with reasonable cost. Then we apply the new approach to study the H₂-O₂ auto-ignition by running millions of simulations. The mechanism of stochastic influence on ignition process will be analyzed thereafter.

2 Simulation Approach

Chemical reactions are caused by collisions of reactant molecules. The reaction speed of a system is determined by molecular collision rate, species concentrations and the probability for a collision leading to a reaction. The reaction events are discrete and at random due to uncertainty in reactive collisions and thermal motion of molecules. If the system is large enough, the reactions can be described using the continuum and deterministic reaction kinetic approach that is applied in combustion at the macroscopic level [5].

Considering a well-stirred system, the discrete and stochastic reaction process can be described by the chemical master equation (CME) which ignores molecular motion and collisions but focuses on the random reaction events:

$$\frac{\partial P(\mathbf{x}, t | \mathbf{x}_0, t_0)}{\partial t} = \sum_{j=1}^M \left[a_j(\mathbf{x} - \mathbf{v}_j) P(\mathbf{x} - \mathbf{v}_j, t | \mathbf{x}_0, t_0) - a_j(\mathbf{x}) P(\mathbf{x}, t | \mathbf{x}_0, t_0) \right]. \quad (1)$$

This equation considers a constant volume system with N species and M reactions. A state vector $\mathbf{X}(t) \equiv (X_1(t), \dots, X_N(t))$ denotes the number of molecules of N species, and for each reaction a state change $\mathbf{v}_j \equiv (v_{1j}, \dots, v_{Nj})$ and a propensity function a_j are used to describe the stochastic reaction kinetics. For a bimolecular reaction of the form $S_1 + S_2 \rightarrow \text{product}(s)$, a_j can be calculated through reaction rate k :

$$a_j = c_j x_1 x_2 = (kV^{-1}) x_1 x_2. \quad (2)$$

Completely solving CME is almost impossible for most reaction systems, but a numerical simulation of one realization can be achieved by using stochastic approach, such as the stochastic simulation algorithm (SSA) proposed by Gillespie [5].

The SSA method generally takes two steps to decide each reaction event in time sequence by setting the next reaction time τ and the index of the next reaction j . A simple implementation to generate these two random values are shown below,

$$\tau = \frac{1}{a_0} \ln \left(\frac{1}{r_1} \right), a_0 = \sum_{i=1}^M a_i, \quad (3)$$

$$j = \text{the smallest integer satisfying } \sum_{i=1}^j a_i > r_2 a_0,$$

where r_1 and r_2 are two random numbers between 0 and 1. The SSA method has a much higher efficiency than other particle simulation methods such as molecular dynamics (MD) and DSMC method because it models events at the time scale of reaction rather than collision. It has been widely used to study cellular systems in biology, and has been applied to simulate the microscopic process of auto-ignition for a premixed methane and air in a volume from $(0.05\mu\text{m})^3$ to $(0.3\mu\text{m})^3$ [4].

While the SSA method can deal with ignition in a small volume, it requires implicit techniques to speedup the simulation efficiency for systems having larger volume. Therefore, the tau-leaping procedure [5] is combined with the explicit SSA method. A couple of other techniques are developed to ensure the smooth transition from SSA to tau-leaping.

The temperature of a mixture is updated by adding a heat releasing process where the system energy is conserved.

3 Results and Analysis

A typical ignition process is shown in Fig.1(a) and several different realizations of identical initial condition are compared in Fig.1(b) where the only difference is the values of random numbers. In this simulation, $T=1200\text{K}$, $n=10^{25}/\text{m}^3$, $V=(1\mu\text{m})^3$ and the mixture is stoichiometric, and the total molecular number is 10^7 . The detailed reaction mechanism [6] is employed to describe the reaction rate. The time history of radicals (H, O, OH) shows obvious fluctuation at early stage because the very few reactant molecules at that moment cause severe uncertainty in chain reactions. Different realizations appear similar processes but with a time shift, which leads to scatter of the ignition delay time.

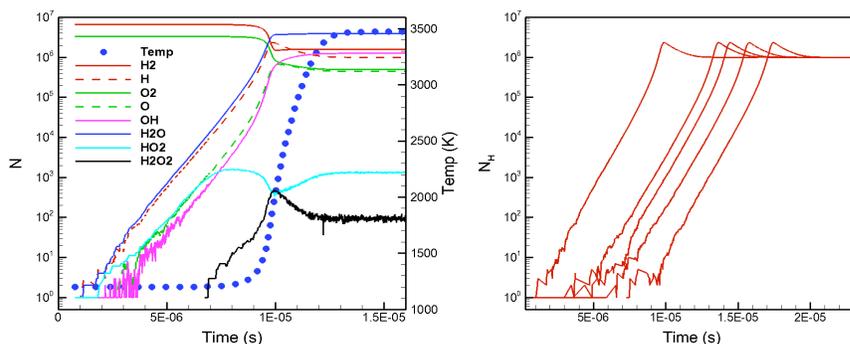


Figure 1. Left: a single SSA realization of auto-ignition process which shows the time history of molecular number for radicals and temperature; Right: a comparison of time history of H molecular number for several realizations. Initial condition is $T=1200\text{K}$, $n=10^{25}/\text{m}^3$, $V=(1\mu\text{m})^3$, and stoichiometric H₂/O₂ mixture.

The fluctuation of species and ignition delay time of the ignition process depends strongly on the temperature and system volume. As the initial temperature decreases, reaction rates drop and the production of radicals slows down, which leads to larger average ignition delay time and its fluctuation. The probability distributions of the ignition delay time are shown in Fig.2, and their standard deviations (STD) are plotted in Fig. 3. Clearly, the STD is very small when the temperature is 1500K, but becomes obvious when it drops to 1200K.

The STD depends also on the volume which is shown in Fig. 4 where the initial temperature is fixed at 1200K. A power law behavior is found at smaller and larger volume regions, and similar result is observed at 900K that is close to the low temperature limit for combustion. This observation can be explained analytically by inspecting the reaction kinetics.

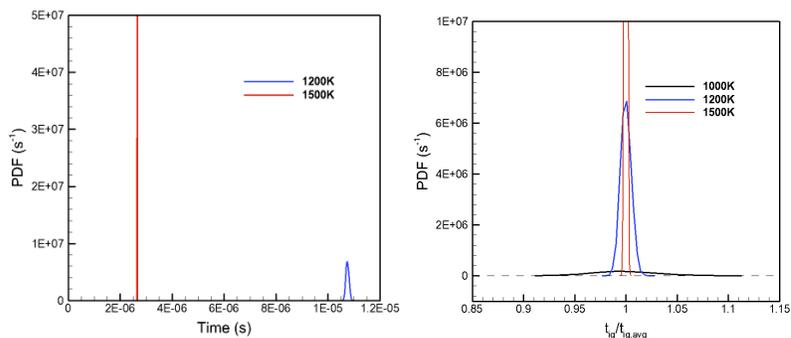


Figure 2. Left: distribution of calculated ignition delay time in absolute time when $T=1500\text{K}$ and 1200K ; Right: distribution of ignition delay time in relative time ($t_{\text{ig}}/t_{\text{ig,avg}}$) when $T=1000\text{K}$, 1200K and 1500K . Other initial condition is $n=10^{25}/\text{m}^3$, $V=(10\mu\text{m})^3$, and stoichiometric H₂/O₂ mixture.

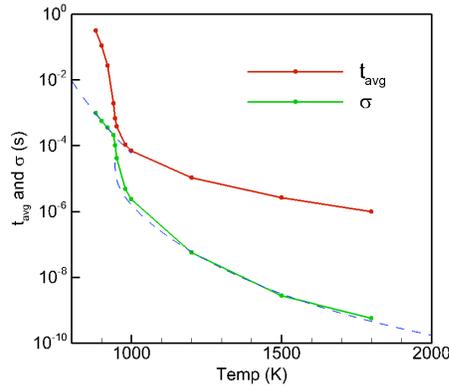


Figure 3. The red line shows the average ignition delay time, the green line shows the standard deviation of ignition delay time, and the dashed line is calculated using the analytical expression in equation (4). Initial condition is $880\text{K} \leq T \leq 1800\text{K}$, $n=10^{25}/\text{m}^3$, $V=(10\mu\text{m})^3$, and stoichiometric H₂/O₂ mixture.

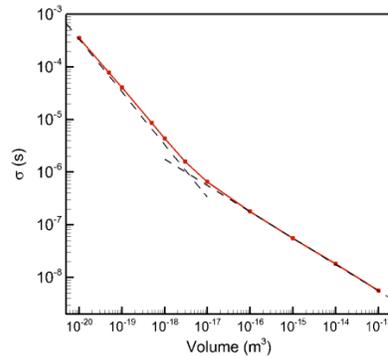


Figure 4. The red line shows the relation between the calculated standard deviation of ignition delay time and system volume, while the dashed line is the approximated power law relation. Initial condition is $T=1200\text{K}$, $n=10^{25}/\text{m}^3$, and stoichiometric H₂/O₂ mixture.

When the volume is sufficiently small, radical initiation is so difficult that this single reaction event dominates the ignition fluctuation. The corresponding fluctuation can be obtained through an exponential distribution and its STD has an expression proportional to $(Vkn_{\text{H}_2}n_{\text{O}_2})^{-1}$, which agrees well with the SSA calculation. When the volume is rather large, both initial reaction and following chain reactions affect the ignition fluctuation. The STD is found to be proportional to $V^{-0.5}$ using a more complicated kinetic analysis with some approximations, which also agrees well with the SSA calculation as shown in Fig. 4.

A more sophisticated expression for the STD estimation is attempted using dimensional analysis. In this analysis, the reduced reaction mechanism [7] is adopted where only 8 key reactions are included. For high temperature ignition, the STD of ignition delay time is mainly determined by the volume and reaction rates of reaction #1 and #2, i.e. $k_1n_{\text{H}_2}n_{\text{O}_2}$ and $k_2n_{\text{H}}n_{\text{O}_2}$. For low temperature ignition, the STD of ignition

delay time is approximately determined by volume and reaction rates of reaction #1 and #7, i.e. $k_1 n_{H_2} n_{O_2}$ and $k_7 n_{HO_2} n_{H_2}$. Combining a non-dimensional relation and the volume dependence of -0.5 power law (not sufficiently small volume), the analytical expression is obtained as:

$$\sigma = \begin{cases} 1.4(k_1 n_1 n_3 (2k_2 - k_5 n_M) n_3 \mathcal{G} T)^{-0.5}, & T > T_{2ed} = 944.2K \\ 1.44(V \mathcal{G} k_1 n_1 n_3 \mathcal{G} k_7 n_1)^{-0.5}, & T < T_{2ed} \end{cases} \quad (4)$$

where the constants are fitted for one case. As shown in Fig. 3, excellent agreement is achieved for the range of temperature from 880K to 1800K while other parameters are default value.

The stochastic nature of reactions influences not only the fluctuation of single realization, but also some macroscopic values in the statistical point of view, such as the average ignition delay time in sufficiently small volume. The reason for this difference between statistical value and its thermodynamic limit may be explained by considering the nonlinear feature of the reaction system. Take reaction #6 ($HO_2 + HO_2 \rightarrow$ Products) as an example, where there are two radicals as reactants. The fluctuation in radicals will cause an increment in the average reaction rate as shown below:

$$\frac{1}{N} \sum (V k n_{HO_2} n_{HO_2}) = \frac{V k}{N} \sum \left[(\bar{n}_{HO_2} + \Delta n_{HO_2})^2 \right] = V k \left[(\bar{n}_{HO_2})^2 + \overline{(\Delta n_{HO_2})^2} \right] = V k (\bar{n}_{HO_2})^2 (1 + \alpha^2) \quad (5)$$

The value of fluctuation influence depends on reaction mechanism. Table 1 shows the results for two reaction mechanisms, which indicates that Boivin's mechanism has a larger value than Saxena's mechanism. As a result the average concentrations of HO_2 and H_2O_2 show difference during the ignition process as shown in Fig. 5.

Table 1: Comparison of α^2 at different time

Mechanism	α^2 at $0.4t_{ig}$	α^2 at $0.6t_{ig}$	α^2 at $0.8t_{ig}$
Boivin ($t_{ig}=0.05$ s)	38.81%	11.97%	22.28%
Saxena ($t_{ig}=0.11$ s)	3.842%	2.624%	3.46%

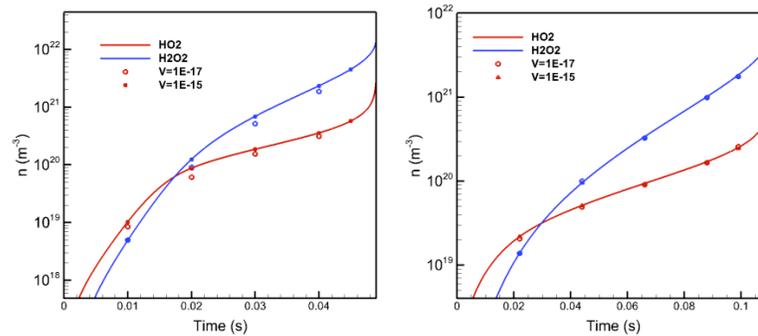


Figure 5. Comparison of radical concentrations of SSA statistical result (dot) and reaction kinetic result (line). Two reaction mechanism (left: Boivin's mechanism; right: Saxena's mechanism) and two volumes ($10^{-17}/m^3$ and $10^{-15}/m^3$) are checked. Initial condition is $T=900K$, $n=10^{25}/m^3$, and stoichiometric H_2/O_2 mixture.

4 Concluding Remarks

The microscopic stochastic nature of chemical reactions influences combustion in both individual realization and statistical behavior. In particular, we derived a detailed expression to estimate the standard deviation of the distribution that is related to the initial temperature and system volume.

It should be mentioned that the present analysis only focuses on the stochastic nature of combustion in micron scale, whereas the molecular motion is neglected. Molecular movement will be important especially for non-uniform system. For uniform system, spontaneous combustion will also lead to non-uniform system. Thus future study may involve molecular motion by developing efficient simulation approaches.

Acknowledgments

This work was supported by the National Natural Science Foundation of China through grants 11372325 and 91116013.

References

- [1] Ju Y. (2014). Recent progress and challenges in fundamental combustion research. *Advances in Mechanics*. 44: 201402.
- [2] Gou X, Sun W, Chen Z, Ju Y. (2010). A dynamic multi-timescale method for combustion modeling with detailed and reduced chemical kinetic mechanisms. *Combust. Flame* 157: 1111.
- [3] Yang C, Sun Q. (2014). Investigation of spontaneous combustion of hydrogen-oxygen mixture using DSMC. *AIP Conference Proceedings*. 1628: 1132.
- [4] Frisque A, et al. (2006). Stochastic simulation of variations in the autoignition delay time of premixed methane and air. *Combustion Theory and Modelling*. 10(2): 241.
- [5] Gillespie DT. (2007). Stochastic simulation of chemical kinetics. *Annu. Rev. Phys. Chem.* 58: 35.
- [6] Saxena P, Williams FA. (2006). Testing a small detailed chemical-kinetic mechanism for the combustion of hydrogen and carbon monoxide. *Combustion and Flame*. 145.1: 316.
- [7] Boivin P et al. (2012) Explicit analytic prediction for hydrogen–oxygen ignition times at temperatures below crossover. *Combustion and Flame*. 159.2: 748.