

Analysis of the Vibrational Non-equilibrium Characteristics in Hydrogen-Oxygen Auto-ignition using DSMC method

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1 Introduction

Thermal-chemical non-equilibrium coupling is an important characteristic in high temperature gas flows. For example, in the extremely high temperature (10000K–20000K) zone behind a re-entry shock, dissociation and thermal relaxation are strongly coupled for the species of air. Besides, in a relatively low temperature (1000K–4000K) range, combustion of hydrogen may also be affected by the thermal-chemical non-equilibrium coupling due to a close time scale of vibrational relaxation and chemical reactions [1].

Based on a quasi-classical trajectory (QCT) calculation of the 3-step chain reactions in hydrogen-oxygen combustion, CFD studies [2, 3] found that in shock-induced combustion such as detonation, the vibrational relaxation of premixed gas reduces the chain reaction rates, therefore leads to a longer auto-ignition delay time and a larger cellular size. Similar results were also obtained by molecular simulation such as the direct simulation Monte Carlo (DSMC) method [4]. Other combustion problems affected by vibrational non-equilibrium include auto-ignition behind reflected shock wave [5] in which vibrational relaxation process influences not only the temperature and pressure behind reflected shock but also the reaction kinetic rates.

Although the influence of vibration relaxation on reaction kinetic was considered in previous work, the complex two-way coupling of thermal and chemical non-equilibrium has not been fully studied. In fact, molecules consumed and produced by elemental reactions are generally thermal non-equilibrium, and their influences on combustion mechanisms as well as the related diagnostic procedure (like the spectrum of excited OH emission [6]) are still unclear at microscopic level.

In order to investigate the vibrational non-equilibrium characteristic of chain reactions and their influence on combustion process, a classical hydrogen-oxygen auto-ignition problem is numerically studied by the

DSMC method in this paper. Simulation algorithm and reaction model are introduced firstly, then numerical results of auto-ignition are analyzed and the thermal non-equilibrium phenomenon is discussed. The conclusion is given at last.

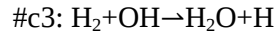
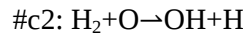
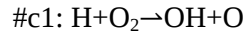
2 Simulation Method and Reaction Model

The DSMC method [7] is a widely applied molecular simulation algorithm for rarefied gas flows and other high temperature thermal-chemical non-equilibrium problems. Unlike molecular dynamics (MD) method, the DSMC method assumes the motions and collisions of molecules can be decoupled within a very small time interval. Under this assumption, phenomenological collision models are used to simulate different kinds of molecular collisions. Among these models, the variable hard sphere (VHS) model, the Larsen-Borgnakke (L-B) model and the total collision energy (TCE) model are mostly used for elastic, inelastic and reactive collisions, which are also used in this paper.

The expression of TCE model can be written as follows

$$P_{\text{reac}} = C_1 \frac{(E_c - E_a)^{C_2}}{E_c^{C_3}}, \quad (1)$$

where E_a is the activation energy, C_1 , C_2 , C_3 are constants determined by molecular properties and Arrhenius form reaction rate. Although TCE model is not a typical vibrationally-favored model, previous studies [4] have shown that it predicts a qualitatively reasonable vibrational non-equilibrium reaction rate of the 3-step chain reactions (#c1-#c3) comparing with a QCT modified two-temperature reaction rate, which means the TCE model is suitable for typical chain exchange reactions with low activation energy.



The vibrational non-equilibrium characteristic not only affects the reaction rate at thermal non-equilibrium state, but also changes the microscopic thermal state during reaction process by consuming and producing molecules with higher vibrational energy. Using the simple harmonic oscillator (SHO) model for vibrational energy, Figure 1 shows the averaged vibrational energy level ($i_{v, \text{avg}}$) of H_2 and O_2 consumed by the 3-step chain reactions at different temperatures. Apparently, they are much larger than the corresponding equilibrium value calculated by the Boltzmann distribution. Converting the averaged vibrational energy level into the corresponding vibrational temperature (T_{vib}) through the equation of SHO model

$$i_{v, \text{avg}} \theta_v = \frac{k \theta_v}{e^{\theta_v/T_v} - 1}, \quad (2)$$

Figure 2 gives a more intuitive result to explain the vibrational non-equilibrium characteristic. For O_2 consumed by #c1 and H_2 consumed by #c2, the rises of vibrational temperature ($\Delta T_{\text{vib}} = T_{\text{vib}} - T_{\text{tr}}$) are about 2000K. For H_2 consumed by #c3, the rise of vibrational temperature is about 1000K, which is much smaller than that of H_2 consumed by #c2.

Although the TCE model is able to describe the non-equilibrium properties of chain reactions, its original form cannot satisfy the detailed balance principle between forward and reverse reactions. Due to the importance of detailed balance in combustion kinetics, different modifications of the TCE model have

been developed. In this paper, a modified reverse reaction model [4] is used which can accurately satisfy the detailed balance. The modified reverse reaction model is as follow

$$\frac{P_{\text{reac},r}(E_{c,r})}{P_{\text{reac},f}(E_{c,f})} = \frac{C_f}{C_r} \cdot \sum_{E_{v,f} < E_{c,f}} \left[\left(\frac{E_{c,f} - E_{v,f}}{kT_{\text{ref}}} \right)^{1.5 - \omega_f + \frac{\xi_{\text{rot},f}}{2}} \right] / \sum_{E_{v,r} < E_{c,r}} \left[\left(\frac{E_{c,r} - E_{v,r}}{kT_{\text{ref}}} \right)^{1.5 - \omega_r + \frac{\xi_{\text{rot},r}}{2}} \right], \quad (3)$$

where C_f and C_r are constants, ω is the temperature exponential coefficient of viscosity, ξ_{rot} is total rotational degrees of freedom in the collision pair, E_v is the total vibrational energy, E_c is the total collision energy. The summation symbol refers to all possible discrete vibrational energy E_v that is smaller than E_c .

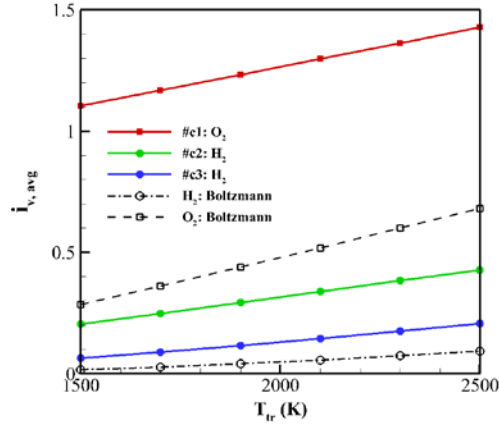


Figure 1. The averaged vibrational energy level of H_2 and O_2 consumed by the 3-step chain reactions.

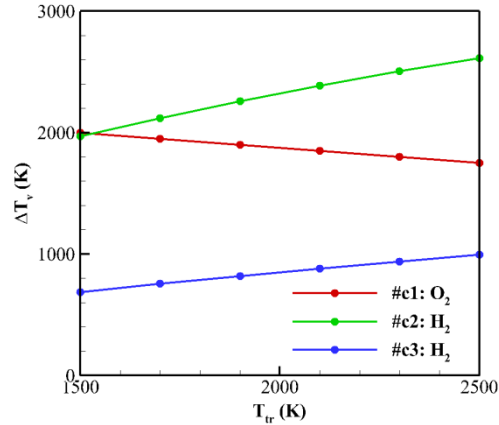


Figure 2. The rises of vibrational temperature of H_2 and O_2 consumed by the 3-step chain reactions.

3 Result and analysis

The H_2 - O_2 auto-ignition is simulated through the DSMC method. A detailed reaction kinetic mechanism [8] of 7 species is used to determine the parameters in the TCE model for forward reactions, and the modified reaction model is used to simulate all reverse reactions. A well-mixed mixture of H_2 and O_2 is filled in a constant-volume box with specular wall condition. The initial condition of the H_2 - O_2 mixture is

$\text{H}_2:\text{O}_2=67\%:33\%$, $T=2500\text{K}$, $n=10^{24}\text{m}^{-3}$ (therefore $p=0.34\text{atm}$), and the total number of simulated particle is 10^6 . Figure 3 shows the DSMC simulation results. The time histories of species concentrations are similar to the reaction kinetic result, but the vibrational temperatures of diatomic (H_2 , O_2 , OH) and polyatomic molecules (H_2O) all deviate from the translational temperature. The decrease of vibrational temperatures of H_2 and O_2 are caused by the consumption of H_2 and O_2 with higher vibrational energy by the 3-step chain reactions, and the accelerating consumption speed during the induction period^[9] finally leads to a significant effect. The slightly higher vibrational temperature of OH is a combined effect of the production (by #c1 and #c2) and consumption (by #c3). The very high vibrational temperature of H_2O is supposed to be caused by the heat release of #c3, and the large amount of energy distributed to the vibrational modes of H_2O molecules results in a slight decrease of translational temperature during the induction period.

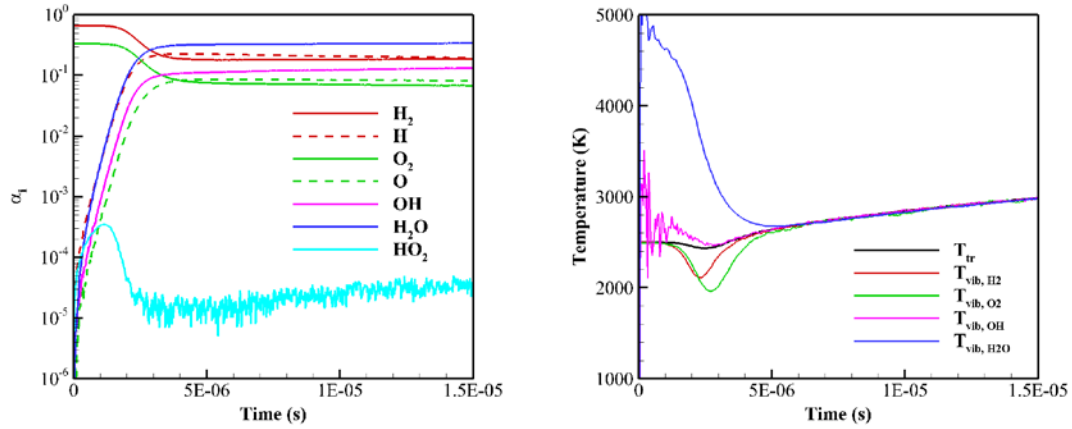


Figure 3. $\text{H}_2\text{-O}_2$ auto-ignition process simulated by the DSMC method. (Left) species concentrations. (Right) translational and vibrational temperatures.

In a chemical reacting system, the evolution of vibrational energy of species k can be described through equation (4),

$$\frac{dE_{v,k}}{dt} = \dot{E}_{relax} + \sum_i \left[\frac{\dot{N}_{\#i,f}}{N_k} (E_{v,f} - E_{v,k}) - \frac{\dot{N}_{\#i,r}}{N_k} (E_{v,r} - E_{v,k}) \right] \quad (4)$$

where $E_{v,k}$ is the averaged vibrational energy of species k , the first part in the right hand side $\dot{E}_{relax}$ is the energy derived from vibrational relaxation and the second part in the right hand side is the energy derived from chemical reactions. Forward reaction (subscript f) is defined as the reaction consuming species k and reverse reaction (subscript r) is defined as the reaction producing species k , $\dot{N}_{\#i,f}$ and $\dot{N}_{\#i,r}$ are the number of reactions occurred per unit time, $E_{v,f}$ and $E_{v,r}$ are the averaged vibrational energy of species k consumed or produced by reactions, N_k is number of molecules of species k . Taking O_2 as an example, by only considering reaction #c1 and its reverse reaction, equation(4) can be simplified as follows,

$$\frac{dE_{v,O_2}}{dt} = \frac{E_{v,eq,O_2} - E_{v,O_2}}{\tau_v} - k_f n_H (E_{v,f} - E_{v,O_2}) + \frac{k_r n_{OH} n_O}{n_{O_2}} (E_{v,r} - E_{v,O_2}). \quad (5)$$

In equation (5), as n_H gradually increases in the induction period, the vibrational temperature of O_2 continuously decreases due to the consumption of higher vibrational energy molecules of O_2 by the forward reaction. As a result of the detailed balance, it will finally be neutralized by O_2 produced by the

reverse reaction. Although the characteristic time scale of vibrational relaxation (τ_v) and chain reaction ($1/(k_f n_H)$) are close at 2500K, the vibrational relaxation term plays a less important role because its averaged effect is much weaker than the effect of the chain reaction.

Figure 4 compares the thermal relaxation term and the chemical reaction terms in equation (4) for H_2 and O_2 based on DSMC simulation results. For H_2 , the moment when the term of reverse reaction catches up with the term of forward reaction almost coincides with the moment when vibrational temperature reaches its minimum value, while term of thermal relaxation only has a very small influence. For O_2 , thermal relaxation still plays a secondary role, but its influence is stronger due to a much fast vibrational relaxation rate. As a result, the vibrational temperature of O_2 reaches its minimum value before the term of reverse reaction catches up with the term of forward reaction.

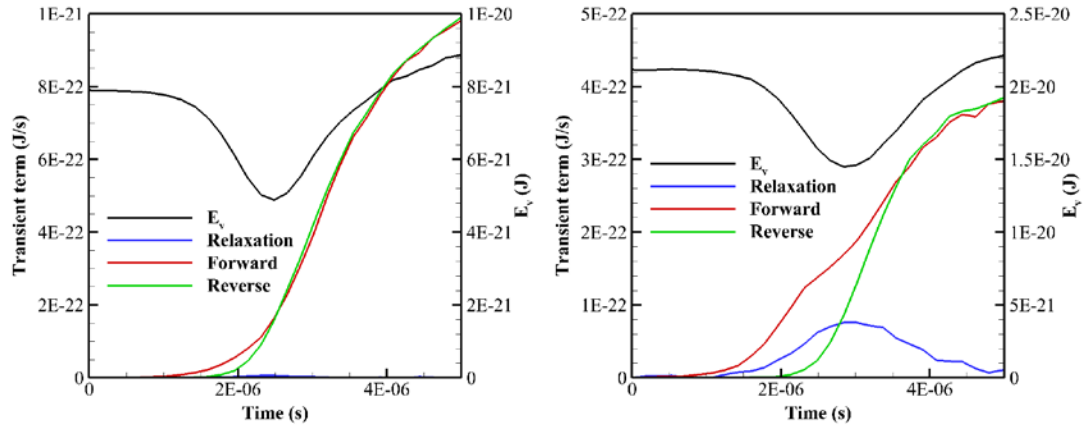


Figure 4 Influence of thermal relaxation and chemical reactions on the averaged vibration energy of H_2 and O_2 . (Left) H_2 ; (Right) O_2 .

The effect of vibrational relaxation will be more important if the temperature decreases or if the mixture is diluted greatly. When initial temperature decreases, vibrational relaxation rate decreases much slower than chain reaction rates. As a result, the decrease of vibrational temperature during auto-ignition process is smaller at lower initial temperature, shown in Figure 5. Theoretically speaking, adding dilution also enhances the influence of thermal relaxation because chemical reaction rate is reduced while thermal relaxation rate doesn't change much. However, even the H_2 - O_2 mixture is diluted by 90% of Ar, the decrease of vibrational temperature is still obvious at an initial condition of $T=2500K$, $n=10^{24} m^{-3}$.

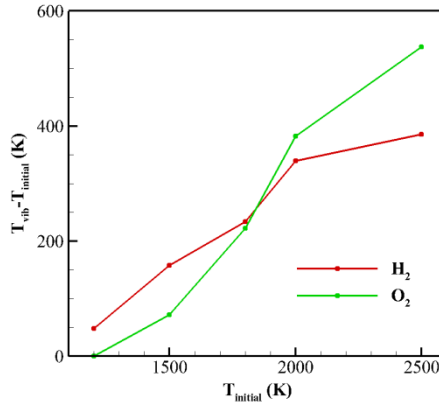


Figure 5. The maximum deviation of vibrational temperatures of H_2 and O_2 from the initial translational temperature.

4 Conclusion

A well-mixed $\text{H}_2\text{-O}_2$ auto-ignition problem is numerically investigated by the DSMC method. The vibrational non-equilibrium characteristic of the 3-step chain reactions is analyzed through the TCE model, and the molecules consumed by chain reactions are found to be at a strong non-equilibrium thermal state. The DSMC results show that the vibrational temperatures of H_2 and O_2 gradually decrease in the induction period, while the vibrational temperature of H_2O is much higher than the translational temperature due to a heat release effect. Theoretical and numerical analysis shows that the variation of vibrational temperature of H_2 and O_2 is mainly affected by the consumption and production of forward and reverse reaction, and vibrational relaxation effect is not important unless the initial temperature is relatively low.

Acknowledgment

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