Effect of Inverse Reactions on One-dimensional Detonation Simulated by DSMC

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1 Introduction

A detonation is a supersonic (with respect to the unburnt fuel) regime of burning in which a strong shock ignites the fuel, which then burns to equilibrium behind the shock, and the energy thereby released helps to drive the shock [1]. Many numerical calculations of detonations have been published [2]. However, correct and fast calculations of the detonation still remain a challenge.

The insight of the propagation structure helps understand the complex mechanism of the detonation, which implies the importance of molecular simulations. The direct simulation Monte Carlo (DSMC) method of Bird [3] is a dominant approach in molecular modeling, which simulates the Boltzmann equation directly. Since all the macroscopic quantities are calculated from the statistics of position and velocity of each simulating particle, DSMC can catch the internal structure more correctly.

Most of the DSMC simulations were based on simple reaction models. Anderson et al. [4] simplify the reaction model in DSMC with a one-step, irreversible, two-species reaction. One-dimensional detonations were simulated and ultrafast ones were obtained. Kulikov et al. [5, 6] carried out one-dimensional DSMC simulations to investigate the gas detonation in the tube initiated by instantaneous heating at the end, who also studied the possibility of physical detonation by vibrationally preexciting the Hydrogen in a shock tube using the same method. While Bondar and Ivanov et al. [7] applied DSMC to the study of detonation in an H2/O2 mixture with detailed chemical kinetics on the basis of effective DSMC molecular chemistry models. The results were in good agreement with the numerical solution of equations of chemical kinetics and yielded C-J velocity and the detonation-wave structure of the Zeldovich - von Neumann - Doering (ZND) theory. However, no analysis of the detonation structure has been made in the view of molecular reaction frequency.

In this paper, the simple reaction model is modified to consider inverse reactions. Keeping the energy release Q and the activation energy E^* for forward reactions constant, we change E^* for inverse reactions in the range of $10.0 - 150.0 kcal/mol$ and compare the difference in detonation-wave structure. The irreversible simulation is also made for the completeness.

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2 Computational method and setup

2.1 The direct simulation Monte Carlo method

The direct simulation Monte Carlo (DSMC) method [3] is now the most effective numerical method for solving the Boltzmann equation. It is superior in modeling flow with nonequilibrium chemical reactions. In a DSMC calculation, simulated particles representing a large number of real atoms or molecules move for a distance according to their velocities in each time step, which is a fraction of the mean collision time. After the particles are indexed, the collision pairs are chosen on a probabilistic basis in each cell, which is also a fraction of the mean free path, and the velocities are redistributed according to kinetic theory. Simulation results are determined by averaging various properties among all particles in each cell and averaging over a large number of ensemble simulations in unsteady DSMC method. This provides a direct numerical solution to the Boltzmann equation and the strong nonequilibrium effects can also be captured precisely by using appropriate cell size and time step. Since the continuum approach may fail when Knudsen number is larger than, generally speaking, 0.01, applying DSMC method to study detonation at samll scales is the first choice.

The DSMC calculations in this paper are performed using our in-house parallel DSMC solver. The variable hard sphere (VHS) model is employed to model the collision process and the no-time-counter (NTC) collision scheme is used, which is the most frequently used collision scheme [3].

The chemical reaction procedure happens right after the collision pairs are chosen. If the relative translation energy is bigger than the activation energy E^*, the reaction happens. In this paper, there are only four reactions with two monatomic species A and B, which are listed below. The masses, molecular diameters and viscosity coefficient of both species are identical, which equals to $8.3 \times 10^{-26} kg$, $3.7 \times 10^{-10} m$ and 0.8 respectively. The energy release and absorption on forward and inverse reactions are fixed at the amount $Q = 8kcal/mol$. The activation energy for forward reactions equals to Q while E^* for inverse ones range from $10kcal/mol$ to $150kcal/mol$.

$$\mathrm{A} + \mathrm{A} \rightarrow \mathrm{A} + \mathrm{B} \tag{1}$$

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{B} + \mathrm{B} \tag{2}$$

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{A} \tag{3}$$

$$\mathrm{B} + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{B} \tag{4}$$

2.2 Computational setup

The computational field is a one-dimensional tube with the top, bottom and right boundary set as specular reflection and the left one set as high-temperature wall ($T_w = 3500K$). The unburned gases are specified as pure A at $100K$, the initial pressure for which is $5000Pa$. By calculating the minimum mean free path and mean collision time in the field, we specify the cell length as $0.25\mu m$ and the time step as $1 \times 10^{-10} s$, which satisfy the requirement. Including an irreversible simulation (i.e. only reaction 1 and 2 exist), there are ten cases in all. The total time steps in each case are about 4000 and twenty time instants during the propagation of detonation are sampled and output. The number of ensemble averages is up to 25000 for all cases.

3 Simulation results

3.1 Detonations with irreversible and reversible reactions

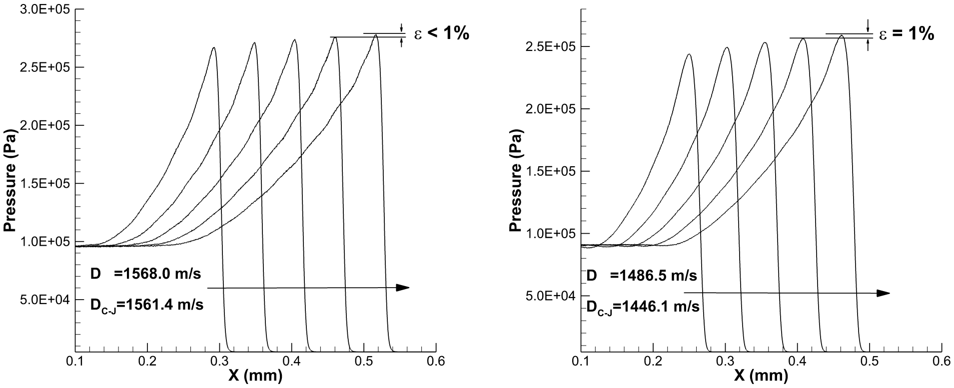

Figure 1: Pressure profiles at different time instants. Left: irreversible model; right: reversible model with $E^* = 25kcal/mol$.

Fig. 1 shows the propagation of detonation in two cases by pressure profiles, where ε denotes the relative error of pressure between the last two profiles, D is the measured propagation velocity and D_{C-J} is the calculated Chapman-Jouguet velocity. A pressure peak immediately behind the shock-wave front is clearly seen. After that, the pressure decreases rapidly to the constant, which is typical for a detonation wave. The wave propagates with an approximately constant velocity and the peak value seems to stabilize, which indicates the stable state of detonation. The measured velocities of two cases are $1568.0m/s$ and $1486.5m/s$. It is easy to understand that the latter is smaller since the endothermic reaction may decrease the released chemical energy which pushes the wave forward.

For the irreversible case, the Chapman-Jouguet velocity can be get according to the initial temperature and Q. The calculated value equals to $1561.4m/s$, which agrees well with the measured one. But for the reversible case, $Q = 8kcal/mol$ can not be substituted into the formula directly since the actual energy release decreases owing to the existence of inverse reaction. The Q we use for reversible case is obtained from the energy conservation equation across the shock listed below, where m is the mass of molecule, u is the macro velocity in the coordinate system which moves with the wave, T is the temperature, k is the Boltzmann constant and 1,2 denote the state upstream and downstream of the shock respectively.

$$Q + \frac{1}{2}mu_1^2 + \frac{5}{2}kT_1 = \frac{1}{2}mu_2^2 + \frac{5}{2}kT_2 \tag{5}$$

u_2 and T_2 can be got by measuring the maximum temperature and macro velocity behind the shock. Together with the known initial state, we can calcuate the Q for the reversible case as $6.84kcal/mol$ and therefore the C-J velocity as $1446.1m/s$, which is a little smaller than the measured one with the error of 2.8%.

3.2 Detonations with different E^*

By changing the activation energy of inverse actions, detonation waves with different measured propagation velocities are obtained. Using the method described before to calculate the Q, we can get Table. 1 which shows the error of maximum temperatures and propagation velocities between the values measured from the result and calculated from C-J condition. Where ε stands for the relative error.

Table 1: Comparison between measured values and theory for reversible cases

Case	E^* (kcal/mol)	Detonation velocity (m/s)	T_2 (k)	ε-velocity (%)	ε-T_2 (%)
1	8	-	-	-	-
2	10	1163.5	1735.3	5.98	-0.62
3	12	1252.8	2217.4	2.94	3.87
4	14	1314.7	2475.9	2.83	5.30
5	16	1362.4	2668.7	2.61	5.41
6	20	1431.4	2938.6	2.72	5.55
7	25	1486.5	3156.4	2.79	5.39
8	100	1560.7	3427.1	3.06	4.50
9	150	1560.7	3428.0	3.00	4.41

All the cases finally come to a stable detonation except case 1 where no detonation forms, and the measured values in Table. 1 are obtained from the stable state. It can be seen that both the detonation wave velocity and maximum temperature climb with the increase of E^*. The relative error for T_2 is arround 5%, which can be attributed to the effect of thermal nonequilibrium that is not taken into account in the C-J theory. And the detonation wave velocity is always a little larger than the C-J velocity, which will be discussed further below based on the sampling of molecular reaction frequency.

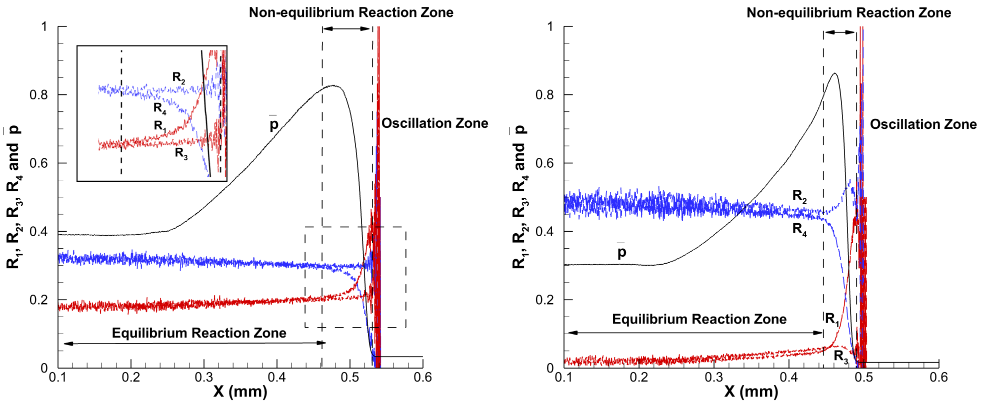

Figure 2: Non-dimensional pressure profile and the detonation wave structure based on molecular reaction frequency. Left: $E^* = 10kcal/mol$; right: $E^* = 25kcal/mol$.

The molecular reaction frequency R_i (i=1, 2, 3, 4, each denotes the corresponding reaction) in Fig. 2 and Fig. 3 is calculated by sampling the number of occurrence of each reaction in the cell at the sampling time instant. To compare the pressure profile and reaction frequency curve in one figure, the non-dimensional pressure is calculated by dividing the pressure by $30kPa$ except for the case of $E^* = 10kcal/mol$, whose pressure is divided by $15kPa$. In Fig. 2,there are three stages of the reaction frequency, the equilibrium reaction zone, the non-equilibrium reaction zone and the oscillation zone, each of which has distinct characteristics. In the first zone, both reversible reactions reach the equilibrium, which means the species fractions keep constant and no energy released. The second zone indicates the fierce chemical reactions happening within because non-equilibrium of reactions exists. Species B and energy continuously come out. While the last zone does not make big sense. Since the reaction frequency is sampled in one time step, the cells in which few reactions happened will have violent oscillation in reaction frequency. The oscillation observed is just the result of reactions of few "high-speed" particles in the nearby cells.

One can observe the decrease of the length of non-equilibrium reaction zone with the increase of E^* for inverse reactions in Fig. 2. If we take the irreversible case as $E^* = \infty kcal/mol$, the relationship between the length and E^* can be plotted considering all the cases exclusive of case 1. And the result (Fig. 3) shows the continuous decrease of the length of non-equilibrium reaction zone with the increase of E^*. This is easy to understand because the higher the threshold for inverse reaction to occur, the faster the converting of A to B and the energy release, resulting in shorter non-equilibrium reaction zone and the more evident von Neumann spike, which is clearly seen in Fig. 2. Together with the relative error for propagation in Table. 1, we can conclude that with the decrease of activation energies for inverse reactions, the detonation wave will propagate faster relative to the C-J velocity, and the non-equilibrium reaction zone will become longer. When the zone becomes too long, the energy released is not concentrated enough to keep the detonation-wave moving, therefore no stable detonation wave forms.

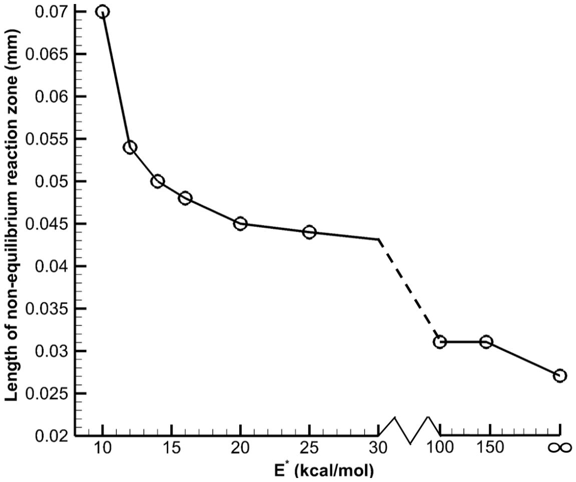

Figure 3: The decrease of length of non-equilibrium reaction zone with the increase of activation energies for inverse reactions.

It should be noted that all the non-equilibrium reaction zones are observed to precede the shock-wave front, which is a little different from the ZND theory (see [8]). So that may be the side effect of the simplified model because the reactions are so easy to happen once the pressure (temperature) is lifted, as is shown in Fig. 2 that the start of the reaction non-equilibrium zone coincides with the lift point of pressure curve. The phenomenon that the fast detonation wave and the overlap of chemical reaction zone with shock wave both exist is similar to that found by Anderson et al. [4]. However, further understand of the relationship between the overlap phenomenon and the fast detonation wave requires more future work.

4 Conclusions

A reversible reaction model is applied to numerically simulate the one-dimensional detonation wave. Only two species A and B, whose properties are idential, are considered. The activation energy E^* for inverse reaction are ranged between $10 - 15kcal/mol$ and the results show that all the cases (except case 1) have a detonation-wave propagation speed a little faster than the C-J velocity when the detonation wave stabilizes. Then the molecular reaction frequency is sampled and calculated. The different zones distinguished by the evident characteristics in reaction frequency curve give a deep insight of the microscopic structure of the detonation wave. And it is concluded that with the decrease of activation energies for inverse reactions, the detonation wave propagates faster relative to the C-J velocity and the non-equilibrium reaction zone becomes longer. When the zone becomes too long, there will be no stable detonation waves. Finally, the side effect of the simplified model is discussed. In the future, we will study the internal relationship between the non-equilibrium reaction zone and the stability or speed of detonation wave.

5 Acknowledgement

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