

Chemical Reaction Mechanism Related Vibrational Nonequilibrium Effect on the Zel'dovich–von Neumann–Döring (ZND) Detonation Model

Ken Chunkit Uy^a, Lisong Shi^a, Chihyung Wen^{a, *}

^aDepartment of Mechanical Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong

Abstract

Discrepancies in detonation cell size are always found between experiments and numerical simulations. The recent numerical simulation by Shi et al. (2016) included the vibrational relaxation effect in molecules and revealed that the vibrational nonequilibrium effect may be one of the reasons for the above discrepancy. In this study, a steady one-dimensional Zel'dovich–von Neumann–Döring (ZND) model is modified to account for the vibrational nonequilibrium effect in gaseous detonation. By introducing a new parameter α , which is defined as the ratio of translational-rotational mode of the specific heat at constant volume to the overall specific heat at constant volume, the translational-rotational energy and the vibrational energy are treated separately in the energy conservation equation. Both the single step and the two step Arrhenius models are used to describe the chemical reaction progress, and the Landau-Teller model and Park's two-temperature model are applied to describe the vibrational energy relaxation and the coupling between the molecular vibration and the chemical reaction, respectively. The parametric study on the modified ZND model is conducted and compared with the conventional ZND one, including the activation energy in chemical model, the ratio of the chemical time scale to the vibrational relaxation time scale and the characteristic vibrational temperature. The results show that the half reaction length is relatively not sensitive to the variation of characteristic vibrational temperature applied in the model (compared with the activation energy and the time ratio), but is increased to a significant extent with the increase of the activation energy and the decrease of the time ratio, when considered the vibrational nonequilibrium. The simulated half reaction lengths in the modified model are in good agreement with those in the conventional model, if the chemical time scale is larger than the vibrational relaxation time scale above a critical ratio when the vibrational nonequilibrium effect is insignificant.

Keywords: Detonation, Vibrational non-equilibrium, ZND model

* Corresponding author. Email address: cywen@polyu.edu.hk, Phone: 27666644

Present address: Department of Mechanical Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong

Nomenclature

C_v	Heat capacity at constant volume
E	Total specific energy
e	Total specific internal energy
$E_{a,i}$	Activation energy for induction model
$E_{a,r}$	Activation energy for reaction model
e_v	Specific vibrational energy
f	Degree of freedom of molecule
k_i	Pre-exponential factor for induction model
k_r	Pre-exponential factor for reaction model
$\mathcal{L}_{1/2}$	Half reaction length
\mathcal{L}_{ind}	Induction zone length
M	Mach number
p	Pressure
Q	Heat of reaction
R	Specific gas constant
T	Temperature
u	Velocity
v	Specific volume
x	Propagation length
Z	Mass fraction of reactant
β	Reaction progress variable for induction model
γ	Specific heat ratio
λ	Reaction progress variable for reaction model (Mass fraction of product)
ρ	Density
τ_c	Chemical reaction time
τ_v	Vibrational relaxation time
$\tau_{1/2}$	Time needed for one half of reactants is consumed under thermal equilibrium condition
τ^*	Time ratio of chemical reaction time to vibrational relaxation time
<i>Superscript</i>	
'	Dimensional form
<i>Subscript</i>	
<i>avg</i>	Geometric average
<i>eq</i>	Thermal equilibrium state
<i>Neq</i>	Vibrational nonequilibrium state

<i>tr</i>	Translation-rotational mode
<i>v</i>	Vibrational mode
<i>vn</i>	von Neumann state
0	Initial reactant state

1. Introduction

Fundamental physics of detonation have been studied for over 100 years. Various engineering application often concerns the safety of gaseous detonation, such as mine gas explosions, combustible gas leakage and the design of fuel devices. A theory estimating the detonation velocity of an explosion mixture was formulated by Chapman and Jouguet in early twentieth century right after the works of Rankine and Hugoniot. The Chapman-Jouguet (CJ) theory aims to provide the appropriate detonation velocity for an explosive mixture at a given initial condition [1]. However, in the mid twentieth century, physicist realized that this simple theory bypasses the details in detonation structure. Those structures are crucial in explaining the propagation mechanism of detonation wave. A theory, which is well known as the Zel'dovich–von Neumann–Döring (ZND) model [2-4], was then proposed to describe specifically the transition processes from reactants to products by a simple chemical model.

Later with the advanced computational power development, numerical studies on the investigation of detonation cellular structures becomes one of the research interest in this area. Researchers have found that there are remarkable discrepancies in cell size and cell patterns between experimental results and numerical simulations [5-7]. Taylor et al. [7] estimated vibrational nonequilibrium effects in detonations by comparing the scale of ignition time and vibrational relaxation time and concluded that the thermodynamic equilibrium assumption may not be always valid. According to their study on stoichiometric H_2 /air detonation at 1 atm and 300 K, the ratio of the ignition delay time to the vibrational relaxation time under the postshock state of 28 atm and 1540 K is less than 3 for H_2 and less than 2 for N_2 for a CJ detonation, assuming that the gas mixture is in thermodynamic equilibrium [8]. The importance of vibrational nonequilibrium effects on the supersonic combustion has also been demonstrated by Voelkel et al. [9] and Koo et al. [10] with detailed chemical reactions. Most recently, Shi et al. [11] conducted the numerical work on $H_2/O_2/Ar$ detonation with both two-temperature and coupled-vibration-chemistry-vibration (CVCV) models to investigate the importance of the vibrational nonequilibrium on the detonation cell size and revealed that the computed detonation cell size is increased when considered the vibrational relaxation. Numerical simulations with the thermal equilibrium assumption on $H_2/O_2/Ar$ detonation using detailed chemistry often gives averaged cell widths lower than the experimental measurement by a factor of 2 [7, 11]. When applying Park's two temperature model and CVCV model in Shi et al. [11], the disparity in cell width has been greatly narrowed down to a factor of 1.33 and 1.32, respectively. Moreover, a clear difference in post-shock state properties between cases under thermal equilibrium and thermal nonequilibrium coupled with chemical reactions is observed.

As well-known, the real detonation case is three dimensional, and the fluid dynamics effect and its coupling with vibrational nonequilibrium must be considered. Nevertheless, in this theoretical study, the historical track of the development of detonation science will be followed. A steady state one-dimensional ZND model will be modified in the first place to include the effects of vibrational energy relaxation and vibrational-chemical coupling on gaseous detonation alone. In this paper, we do not intend to directly predict the detonation cell width, but we aim at exploring the physics behind the disagreement between numerical studies and experimental measurements. Although the role of vibrational nonequilibrium effect on detonation has been assessed by numerical simulations in recent years, only few theoretical effort has been done to show how this effect can be manifested in the classic theory. Tarver was the first one to extend the ZND theory to include the thermal relaxation processes in 1980s [12-14]. This theory is named as the nonequilibrium ZND (NEZND) theory and was extended to liquid and solid explosives for self-sustaining detonation [15]. However, the step-by-step thermal equilibrium assumption made in the NEZND theory on different energy zones may not be always valid particularly in gaseous detonation. The recent works [9-11] have manifested the importance of the vibrational-chemical coupling effect in the gaseous detonation process. To this end, we take the vibrational relaxation into account based on the classic one-dimensional ZND model in different approach with that in Tarver's work. The chemical models and the vibrational relaxation model are taken to be the simplest forms to simplify the theoretical model derivation. Because of the one-dimensionality of the ZND model, results are presented by comparing the half reaction thicknesses instead of the cell sizes in both vibrational equilibrium and nonequilibrium cases. On the direct relation between the half reaction length and the cell size, a detail discussion can be found in Gavrikov et al. [16]. The parametric study is then conducted and the criteria to consider the vibrational nonequilibrium is discussed.

2. Formulation and Modeling

The classic ZND model describes the transition zone between the upstream and downstream states by a chemical process. Reactants are heated and compressed adiabatically once encountered the leading shock. Active radical species are generated in the induction zone right after the shock. When sufficient amounts of radical species are produced, rapid chain-branching reactions take place and products are formed. During this process, chemical energy is released in the form of heat, which drives up the temperature and brings a drop in pressure and density in the reaction zone. The detailed derivation of the steady one-dimensional ZND solution can be found in Fickett and Davis [17].

Molecules consists of translational, rotational, vibrational and electrical energy

mode [18]. Due to the fact that vibrational equilibrium requires thousands of collisions whereas translational-rotational equilibrium can be established in less than 20 molecular collisions [7], the former becomes an important concern in high temperature flow over 600 K. At the detonation front, the temperature reaches to thousands of Kelvin. However, in the past, thermal equilibrium related to the four energy modes are often assumed when considering the detonation propagation. This is the possible reason why discrepancies in detonation cell size are always found between experiments and numerical simulations. Recently, several researchers conducted numerical simulations regarding vibrational relaxation effect in molecules and discovered that the ignorance of this effect may be one of the reasons [7, 8, 11, 19]. A modified ZND model is thus proposed to investigate the vibrational nonequilibrium effect. While ignoring viscous effects and electrical energy mode, the corresponding steady one-dimensional conservation equations are given by

$$\frac{d}{dx}(\rho u) = 0, \quad (1)$$

$$\frac{d}{dx}(p + \rho u^2) = 0, \quad (2)$$

and

$$\frac{d}{dx}[(\rho E + p)u] = 0, \quad (3)$$

where

$$E = e + \frac{u^2}{2} = \frac{p}{\rho(\gamma-1)} - \lambda Q + \frac{u^2}{2} = \frac{\alpha p}{\rho(\gamma-1)} + e_v - \lambda Q + \frac{u^2}{2}, \quad (4)$$

$$e_v = \frac{\theta/T_v}{e^{\theta/T_v}-1} RT_v, \quad (5)$$

$$\alpha = \frac{C_{v,tr}}{C_{v,tr} + C_{v,v} \frac{T_v}{T_{tr}}}, \quad (6)$$

$$C_{v,tr} = \frac{f}{2} R, \quad (7)$$

$$C_{v,v} = \left(\frac{\partial e_v}{\partial T_v} \right)_{const. vol} = R \frac{(\theta/T_v)^2 \exp(\theta/T_v)}{[\exp(\theta/T_v)-1]^2}. \quad (8)$$

The specific heat ratio, γ , is assumed to be constant during the detonation process. The degree of freedom f is thus evaluated by $f = 2/(\gamma - 1)$, based on its relation with γ . The major change compared with the conventional ZND model is that the internal

energy is separated into two parts in energy equation, Eq. (4), i.e. $\alpha p/\rho(\gamma - 1)$ for the translational-rotational energy and e_v . α is defined as the comparison between translational-rotational energy and the total internal energy in terms of specific heats at constant volume C_v , where $C_{v,tr}$ and $C_{v,v}$ are defined accordingly from the viewpoint of statistical thermodynamics [18]. In other word, the ratio of the translational-rotational energy to the vibrational energy may vary during the detonation process, while the total energy is conserved. The characteristic vibrational temperatures of different molecules are listed in Table 1.

Table 1 Characteristic vibrational temperature of molecules from Shi et al. [11].

Molecules	θ (K)
H ₂	5989
O ₂	2250
OH	5140
HO ₂	1577, 2059, 5325
H ₂ O	2297, 5266, 5409

Single step Arrhenius equation is commonly used to describe the change of reaction progress variables λ across the one-dimensional ZND profile [1, 20, 21], i.e. in Eq. (4) and is expressed below:

$$\frac{d\lambda}{dt} = k_r(1 - \lambda)\exp\left(\frac{E_{a,r}}{T}\right), \quad (9)$$

The validity of the single step mechanism in detonation problems can be found in Kessler et al. [22].

If a thermal neutral chain-branching induction zone is also considered between the shock front and the reaction zone, a parameter β representing the reaction progress variable for induction zone can be formulated by another temperature-dependent Arrhenius equation as discussed by Short & Sharpe [23] and Jian et. al. [24] and is shown below:

$$\frac{d\beta}{dt} = k_i\beta\exp\left(E_{a,i}\left(\frac{1}{T_{vn}} - \frac{1}{T}\right)\right), \quad (10)$$

where T_{vn} is the von-Neumann temperature at shock front and can be evaluated from the equilibrium Rankine-Hugoniot relation, with the given γ and Q . β equals to 0 at the start of induction zone (right behind shock front) and increases to the value of 1 at

the end of the zone across the profile. Once the limit of $\beta = 1$ is reached, exothermic reaction starts in the next stage, which is governed by Eq. (9). The induction zone length \mathcal{L}_{ind} is thus defined in the region where $0 \leq \beta \leq 1$. Temperature T in Eq. (9) and Eq. (10) is replaced by an averaged temperature T_{avg} to consider the coupling between the vibrational nonequilibrium effect and the chemical reaction. As discussed by Park [25], the averaged temperature T_{avg} is shown as

$$T_{avg} = \sqrt{T_{tr}T_v} \quad (11)$$

The Landau-Teller model in Eq. (12) was applied to describe the energy transfer rate S_{tr-v} between the translational-rotational energy and the vibrational energy. e_v in Eq. (4) is thus updated across the profile based on this vibrational relaxation mechanism.

$$S_{tr-v} = \rho \frac{e_v^{eq} - e_v}{\tau_v}, \quad (12)$$

where e_v^{eq} is the vibrational energy at equilibrium state, i.e. when vibrational temperature T_v is equal to translational-rotational temperature T_{tr} . τ_v is the vibrational relaxation time and can be expressed by the existing empirical model by Millikan and White [26]. Since the calculation of vibrational energy e_v requires the input of vibrational temperature T_v at corresponding position, the value of T_v can be obtained through Newton's Iteration between each position intervals.

By these equations, the nonequilibrium Rankine-Hugoniot relation can be constructed. It combines the initial energy state at the low temperature range (the vibrational state is not excited) and the vibrationally excited energy state. The relation is derived as follows:

$$u^2 = v^2 \frac{p-p_0}{(v_0-v)}, \quad (13)$$

$$(\alpha p v - p_0 v_0) \frac{1}{\gamma-1} + \frac{1}{2}(p + p_0)(v - v_0) + e_{vib} - \lambda Q = 0, \quad (14)$$

The unburned state is described as below after nondimensionalization,

$$\rho_0 = p_0 = T_0 = 1, u_0 = \sqrt{\gamma}M_0, e_0 = \frac{1}{\gamma-1}. \quad (15)$$

Equating Eq. (13) and Eq. (14) gives the new ZND solution in terms of p and ρ as shown below:

$$\rho = \frac{M^2(\gamma + 1 + 2\varsigma)}{(\gamma M^2 + 1)(1 + \frac{\varsigma}{\gamma})[1 \mp w_\rho(\varsigma)\xi(\lambda, e_v, \varsigma)]} \quad (16)$$

$$p = \frac{(\varsigma + 1)(\gamma M^2 + 1)}{(\gamma + 1 + 2\varsigma)} [1 \pm \gamma w_p(\varsigma)\xi(\lambda, e_v, \varsigma)] \quad (17)$$

$$\varsigma = \alpha - 1 \quad (18)$$

$$w_\rho(\varsigma) = \frac{M^2 - 1}{(\gamma M^2 + 1)(1 + \frac{\varsigma}{\gamma})} \quad (19)$$

$$w_p(\varsigma) = \frac{M^2 - 1}{(\gamma M^2 + 1)(\varsigma + 1)} \quad (20)$$

$$\xi(\lambda, e_v, \varsigma) = \sqrt{1 - \frac{\lambda Q}{\Omega(\varsigma)} + \frac{e_v}{\Omega(\varsigma)} + \frac{\varsigma^2}{\Phi_1} + \frac{\varsigma}{\Phi_2}} \quad (21)$$

$$\Omega(\varsigma) = \frac{\gamma(M^2 - 1)^2}{2M^2(\gamma^2 - 1 + 2\varsigma(\gamma - 1))} \quad (22)$$

$$\Phi_1 = \frac{\gamma^2(M^2 - 1)^2}{(\gamma M^2 - 1)^2} \quad (23)$$

$$\Phi_2 = \frac{\gamma(M^2 - 1)^2}{2(\gamma M^4 + 1)} \quad (24)$$

The two roots with negative and positive signs in Eq. (16) (positive and negative signs in Eq. (17), correspondingly) indicate the strong and weak detonation solution, respectively. In this paper, strong detonation solution is presented. The physical quantities in Eq. (15) to (24) are nondimensionalized with respect to the state of the unburned reactants as follows:

$$\begin{aligned} \rho &= \frac{\rho'}{\rho_0}, p = \frac{p'}{p_0}, T = \frac{T'}{T_0} = \frac{\rho_0 RT'}{p_0}, u = \frac{u'}{\sqrt{RT_0}} \\ x &= \frac{x'}{x_0}, t = \frac{t'}{x_0/\sqrt{RT_0}}, k_i = \frac{k'_i}{\sqrt{RT_0}/\mathcal{L}_{ind}}, k_r = \frac{k'_r}{\sqrt{RT_0}/x_0} \\ E &= \frac{E'}{RT_0}, E_{a,i} = \frac{E_{a,i}'}{RT_0}, E_{a,r} = \frac{E_{a,r}'}{RT_0}, Q = \frac{Q'}{RT_0} \end{aligned} \quad (25)$$

\mathcal{L}_{ind} and x_0 are the induction zone length and the half reaction length of the

equilibrium case respectively. Half reaction length is defined as the region where λ increases from 0 to 0.5, i.e. half of the initial reactant is consumed.

Having a close look at the square root term $\xi(\lambda, e_v, \zeta)$ in Eq. (21) and comparing it with that in the original ZND expression [20, 27], extra terms $e_v/\Omega(\zeta)$, ζ^2/Φ_1 and ζ/Φ_2 are presented. This implies that the newly established ZND model does not only include the chemical reaction effect, i.e. $\lambda Q/\Omega(\zeta)$, but also the vibrational relaxation effect to evaluate the thermodynamic variables along the detonation wave propagation.

At the beginning of chemical reaction (i.e. $\lambda = 0$) where vibrational energy state is not yet excited, i.e. $\alpha = 1$ and thus $\zeta = 0$, $\lambda Q/\Omega(\zeta)$, ζ^2/Φ_1 and ζ/Φ_2 in Eq. (21) are zero. e_v is a function of T_v (Eq. (5)) and T_v is equal to T_0 at this stage. Since value of e_v is much less than unity, $\xi(\lambda, e_v, \zeta)$ can be considered to be 1. As the chemical reaction goes on, λ goes to 1 at the end of reaction. Thermodynamic properties ρ and p in Eq. (16) and (17) becomes constant after the end of reaction as the CJ state is reached. Therefore, $\xi(\lambda, e_v, \zeta)$ at the CJ state is zero. In the conventional ZND profile [20, 27], the value of ξ is always between 0 and 1, which indicates the end and the beginning of the chemical reaction, respectively. This conclusion is physically valid for $\xi(\lambda, e_v, \zeta)$ in the modified ZND profile too. Figure 1 shows the typical variations of λ and ξ along the ZND profile.

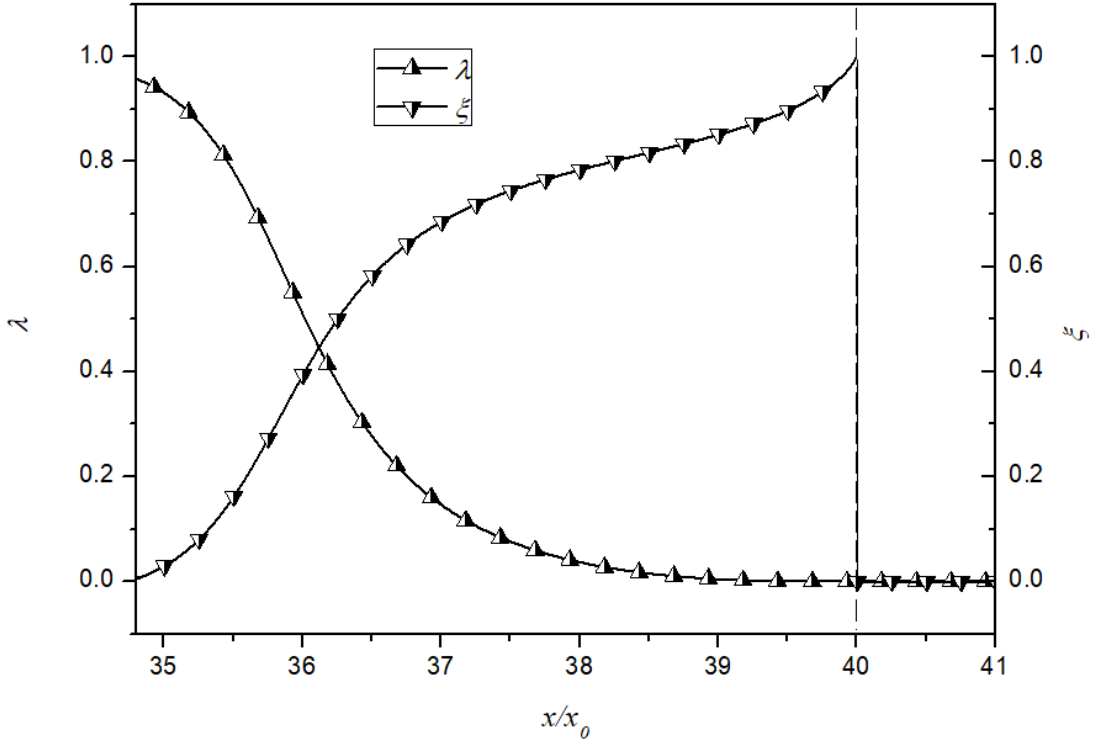


Fig. 1. Variations of λ and ξ along the ZND profile with $\gamma = 1.2$, $Q = 50$, $E_{a,r} = 50$ at $\tau^*=0.25$ and $\theta=2250$ K for the nonequilibrium case (one of the test cases in section 3.1 later). The shock is encountered at $x/x_0 = 40$ and reaction starts right after the shock. As seen, ξ approaches zero gradually when λ is advancing to 1.

On the other hand, vibrational relaxation continues even the chemical reaction is finished. Through the exchange of energy, T_v will eventually catch up with T_{tr} and thus e_v increases. Ratio α decreased across the ZND profile accordingly. At the state when vibrational equilibrium is reached, i.e. $T_v = T_{tr}$, α becomes constant and $\alpha < 1$ is therefore always valid across the profile.

Quantities along the profile were obtained through direct integration across the profile. To facilitate the parametric study in the later section, a time scale ratio $\tau^* \equiv \tau_{1/2}/\tau_v$ is introduced to compare the characteristic chemical reaction time $\tau_{1/2}$ with the vibrational relaxation time. In this study, $\tau_{1/2}$ is defined as the time needed for one half of the reactants is consumed in the reaction under the thermal equilibrium condition. The definition of time ratio τ^* is crucial as it reveals the condition under which the vibrational nonequilibrium effect is significant in gas detonation problem.

3. Results and Discussion

Based on the modified one-dimensional ZND solution presented in the previous section, how the key parameters in the formulation affect the half reaction length $\mathcal{L}_{1/2}$ in both the thermal equilibrium and nonequilibrium cases are investigated systematically. Following the previous studies on conventional ZND solution [17, 21, 28, 29], parameter settings are summarized in Table 2. The length of the domain of interest is $1000 \mathcal{L}_{1/2}$. Over 200 mesh points was used per half reaction length in the integration of ZND profile in each case.

Table 2 Parameters used in the modified ZND profile simulations

Parameter commonly used in both conventional and modified ZND model	
γ	1.2
Q	50
k_i	17
k_r	2400
Parameter used in modified ZND model only (vibrational nonequilibrium case)	
T_0	300 K
R	259.8 J/kg K

Initial temperature T_0 and gas constant for oxygen R were given such that e_v and other parameters can be nondimensionalized in Eq. (5) and Eq. (25), respectively, across the profile. These parameter values of T_0 and R were chosen following those in $\text{H}_2/\text{O}_2/\text{Ar}$ detonation by Shi et al. [11].

Parametric study presented in this section are divided into four parts. For the first

three parts which considered the single step Arrhenius model, different values of the non-dimensional parameters– activation energy $E_{a,r}$, time ratio τ^* and characteristic vibrational temperature θ were tested while keeping other settings constant. Since γ and Q only change the initial (reactant) state and the end (product) state properties but not the detonation structure in the transition zone (i.e. the gradient of the profile and thus the half reaction length), these values were kept constant throughout the analysis. The critical τ^* at which the vibrational nonequilibrium effect should be considered is discussed.

However, reactions where chain-initiation stage is comparably important cannot be represented effectively in single step Arrhenius model [30]. Therefore, in the last part, a two step Arrhenius chemical model with combination of both induction zone model, i.e. Eq. (10) and the reaction model, i.e. Eq (9) is investigated. The critical τ^* again is discussed while keeping the ratio of $\mathcal{L}_{1/2}$ and \mathcal{L}_{ind} and to be 2:1 under the thermal equilibrium state. Through these single step and two step simplified models from detailed chemistry, a physical picture of how the vibrational nonequilibrium effect can play a role in temperature-dependent reaction models in gaseous detonation will be illustrated.

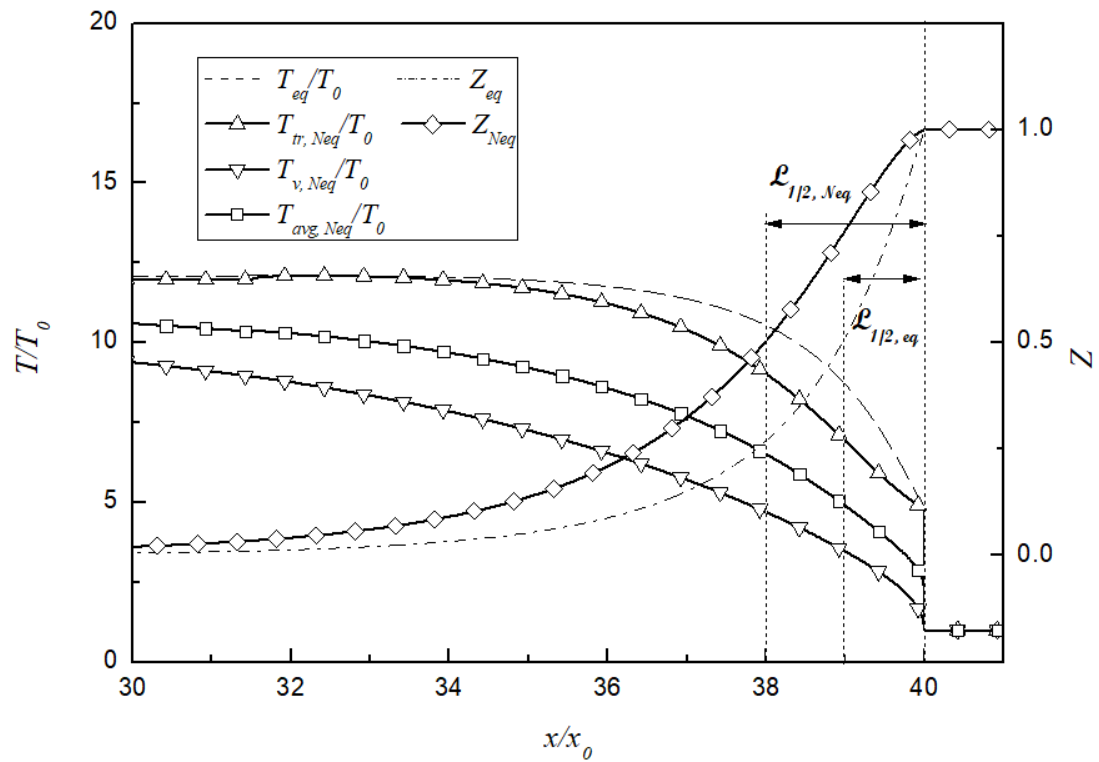
3.1. Dependence on activation energy using single step Arrhenius model

Activation energy $E_{a,r}=10, 20, 30, 40$ and 50 were selected to be examined its effect on the detonation when the vibrational nonequilibrium is significant in this section. Notably, in $\text{H}_2/\text{O}_2/\text{Ar}$ detonation, oxygen is one of the crucial reactants in the simulations. Therefore, $\theta=2250$ K for oxygen molecules from Table 1 was selected in evaluating the vibrational energy term e_v . The time ratio $\tau^*=0.25$ was selected to have a value less than unity such that the vibrational relaxation time scale is longer than the chemical reaction time scale across the profile. The vibrational nonequilibrium effect is thus dominant in this manner to address its effect.

Fig. 2 shows the profiles of temperature ratio T/T_0 and mass fraction of reactant Z for cases with $E_{a,r}=10$ and $E_{a,r}=50$. Comparing the case of $E_{a,r}=10$ in Fig. 2 (a) with the case of $E_{a,r}=50$ in Fig. 2 (b), the half reaction length in the nonequilibrium case of $E_{a,r}=50$ is much longer, with a much flatten slope in the Z curve initially. The half reaction length in the nonequilibrium case of $E_{a,r}=50$ is $4\mathcal{L}_{1/2}$ (4 times that of the half reaction length in the equilibrium case) and is double that in the nonequilibrium case of $E_{a,r}=10$. Although the chemical model applied in the formulation is one-step reaction without any induction time model, i.e. Eq. (9), it provides a clue that the reaction is much slower initially in the vibrational nonequilibrium case compared with that in the equilibrium case. The possible explanation is that the excitation of vibrational mode in molecules reduces the effective reaction temperature for the chemical reaction.

In the beginning of the reaction right after the shock (i.e. $x/x_0 < 40$), there is a large difference between translational-rotational temperature T_{tr} and vibrational temperature T_v . As the relaxation process goes on, T_v approaches to T_{tr} gradually. This can be manifested by the Park's two temperature model in the reaction modeling, where T_{avg} has a close value to T_{tr} eventually in the end of reaction. The features of the profiles match with that of the one dimensional numerical simulation by Shi et al. [11].

a



b

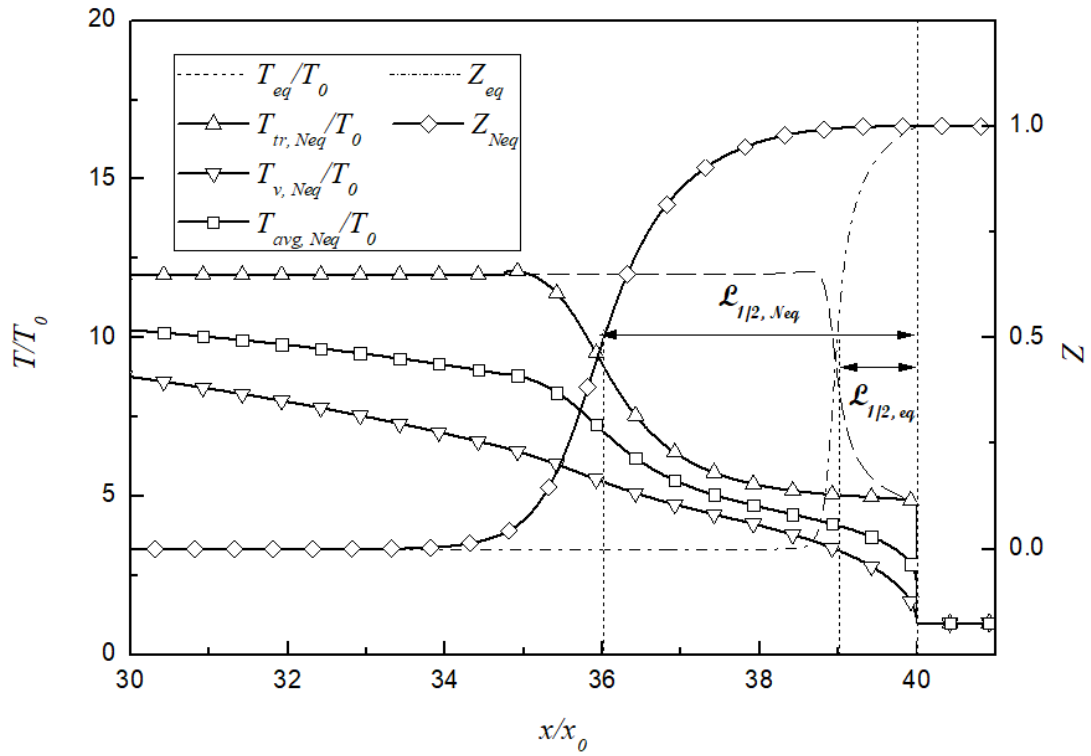


Fig. 2. Temperature ratio T/T_0 and mass fraction of reactant Z profiles at the vibrational equilibrium state (eq) and the vibrational non-equilibrium state (Neq) using single step Arrhenius model with (a) $E_{a,r}=10$ and (b) $E_{a,r}=50$ at $\tau^*=0.25$ and $\theta=2250$ K.

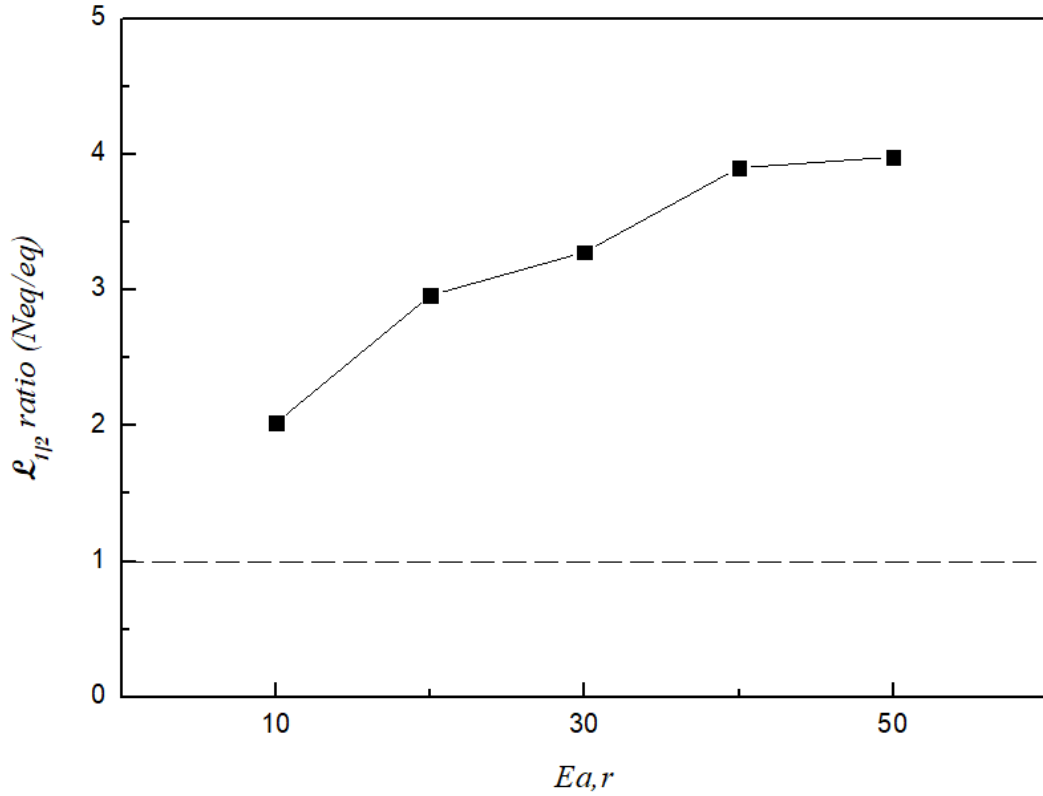


Fig. 3. Ratio of $\mathcal{L}_{1/2}$ for the nonequilibrium case to that of the equilibrium case versus $E_{a,r}$ at $\tau^*=0.25$ and $\theta=2250$ K.

The ratio of half reaction length under the vibrational nonequilibrium (*Neq*) assumption to that under the vibrational equilibrium (*eq*) assumption (i.e. take the equilibrium $\mathcal{L}_{1/2}$ unity as reference) versus the selected $E_{a,r}$ values is presented in Fig. 3. As shown, the half reaction length under the vibrational nonequilibrium assumption is at least twice that under the vibrational equilibrium assumption. The ratio can be up to four times to that of the equilibrium $\mathcal{L}_{1/2}$ if high activation energy is selected in the chemical model formulation. The degree of increased $\mathcal{L}_{1/2}$ ratio may vary with the choice of the initial state properties, such as γ and Q , but the trend of having longer $\mathcal{L}_{1/2}$ with higher activation energy input under the vibrational nonequilibrium assumption stands. This suggests that the vibrational relaxation becomes an even more important concern when the chemical reaction with high activation energy is involved in the gas detonation problem.

3.2 Dependence on time ratio of chemical reaction time scale to vibrational relaxation time scale using single step Arrhenius model

Under the vibrational nonequilibrium consideration, not only chemical reaction time scale $\tau_{1/2}$ but also the vibration relaxation time scale τ_v is involved in the

problem. Taylor et al. [7] has computed the ignition delay time τ_{ign} in H₂-air detonation and compared τ_{ign} with that of vibrational relaxation time of H₂ equilibrating in H₂, $\tau_{H_2-H_2}^{vib}$. Their results revealed that τ_{ign} is less than 10 $\tau_{H_2-H_2}^{vib}$ in most detonation simulations. Therefore, different time ratios $\tau^* = \tau_{1/2}/\tau_v = 0.25, 0.5, 1, 2, 3, 4, 5, 6$ and 7 were tested to investigate how the calculated half reaction length varies in different nonequilibrium conditions. Fig. 4 shows the variation of the half reaction length $\mathcal{L}_{1/2}$ ratio defined in section 3.1 with the selected time ratio τ^* at $E_{a,r}=50$ and $\theta=2250$ K. As seen, $\mathcal{L}_{1/2}$ ratio becomes closer to unity as the time ratio τ^* increases and vice versa. When the chemical time scale $\tau_{1/2}$ is sufficiently large compared with the vibrational relaxation time scale τ_v , the molecular vibrational state approaches to its equilibrium condition. Consequently, the calculated half reaction length approaches to the equilibrium solution. On the other hand, when $\mathcal{L}_{1/2}$ is larger than one, the vibrational relaxation time scale τ_v is larger than the chemical time scale $\tau_{1/2}$. The flow is under significant vibrational nonequilibrium. The extraction of vibrational energy from the translational energy reduces the effective reaction temperature for the chemical reaction and extends $\mathcal{L}_{1/2}$ accordingly.

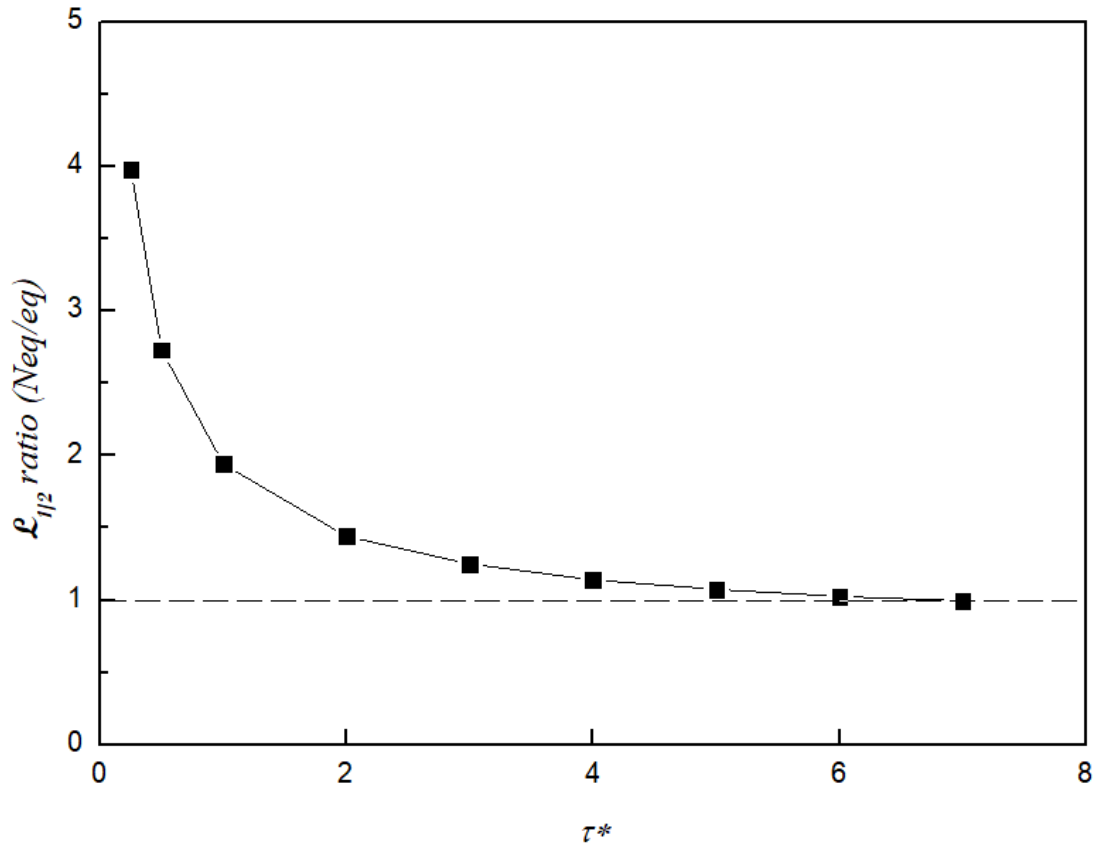


Fig. 4. Ratio of $\mathcal{L}_{1/2}$ for the nonequilibrium case to that of the equilibrium case versus τ^* at $E_{a,r}=50$ and $\theta=2250$ K.

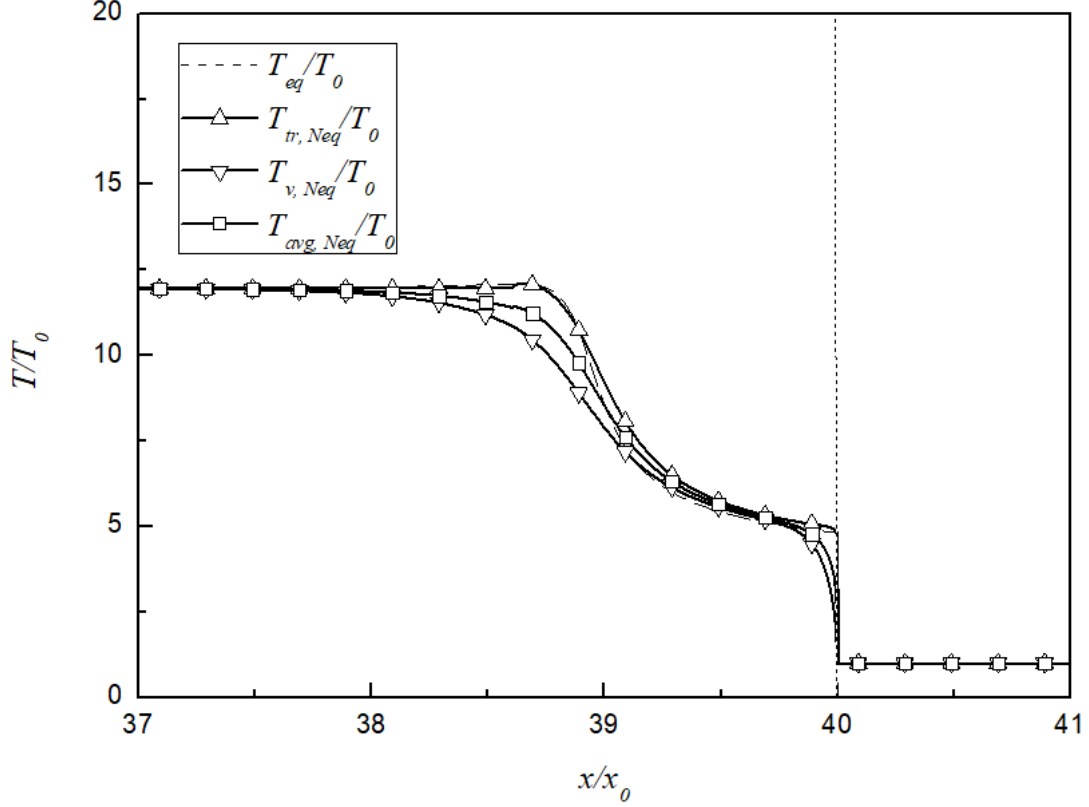


Fig. 5. Temperature ratio T/T_0 and mass fraction of reactant Z along the ZND profile using single step Arrhenius model in the case of $\tau^*=7$ at $E_{a,r}=50$ and $\theta=2250$ K.

Taking $\tau^*=7$ as an example, Fig. 5 illustrates the large τ^* case where vibrational equilibrium is quickly established at the start of reaction. Vibrational temperature T_v raises closely with T_{tr} along the reaction. According to the Park's two temperature model [25] in Eq. (23), averaged temperature T_{avg} is expected to have close values with the temperature input in conventional ZND profile under the selected τ^* . Therefore, $T_{avg,Neq} \approx T_{eq}$ and similar temperature values were input in the single step chemical model. Results of $\mathcal{L}_{1/2}$ calculations in both the conventional ZND solution and the modified ZND solution are then expected to be the same, as shown in Fig. 3. This further provides the proofs that the current modified ZND solution is not only capable of calculating the properties with the vibrational nonequilibrium effect but also the properties in under conventional equilibrium assumption.

It is noted that the empirical model of Millikan and White [26] for the vibrational relaxation time estimation requires the input of reduced mass evaluated from the molecular masses in the tested mixture, and temperature and pressure in the corresponding time step. In other words, the vibrational relaxation time changes along the profile right after the shock, but the variation is within the same order accuracy in the gas detonation simulation. The demonstration of constant τ^* cases here is therefore

a reasonable analysis for the parametric study with the modified ZND model. In summary, under the given parameter settings here, the critical τ^* at which the vibrational nonequilibrium effect is important is suggested to be $\tau^* \leq 7$.

3.3 Dependence on characteristic vibrational temperature θ using single step Arrhenius model

Regarding to Table 1, the variation in the characteristic vibrational temperature θ can be up to thousands of Kelvin. With $\theta=2250$ K, i.e. the data related to O_2 , for easier demonstrations in section 3.1 and 3.2, one may argue that those results are also sensitive to θ . Therefore, a set of θ is tested in this section from 2000 K to 6000 K with increased intervals of 1000 K in each trial.

Fig. 6 shows the variation of $\mathcal{L}_{1/2}$ ratio with θ at $E_{a,r}=50$ and $\tau^*=0.25$. As mentioned in section 3.1 Dependence on activation energy, $\tau^*=0.25$ was chosen so that the vibrational relaxation time scale is longer than the chemical reaction time scale across the profile to address the vibrational nonequilibrium effect. In the selected θ ranges, the variation of $\mathcal{L}_{1/2}$ ratio is within unity and decreases with the increasing θ . Although the $\mathcal{L}_{1/2}$ ratio decreases up to 20 % when θ increases from 2000 K to 6000 K under vibrational nonequilibrium conditions, it is relatively not sensitive to θ , compared with $E_{a,r}$ and τ^* . Fig. 7 compares the results of $\theta=6000$ K with the results of $\theta=2250$ K in section 3.2. Similarly, increasing θ will bring down the $\mathcal{L}_{1/2}$ ratio under the same τ^* and the $\mathcal{L}_{1/2}$ ratio approaches unity when $\tau^* \geq 7$.

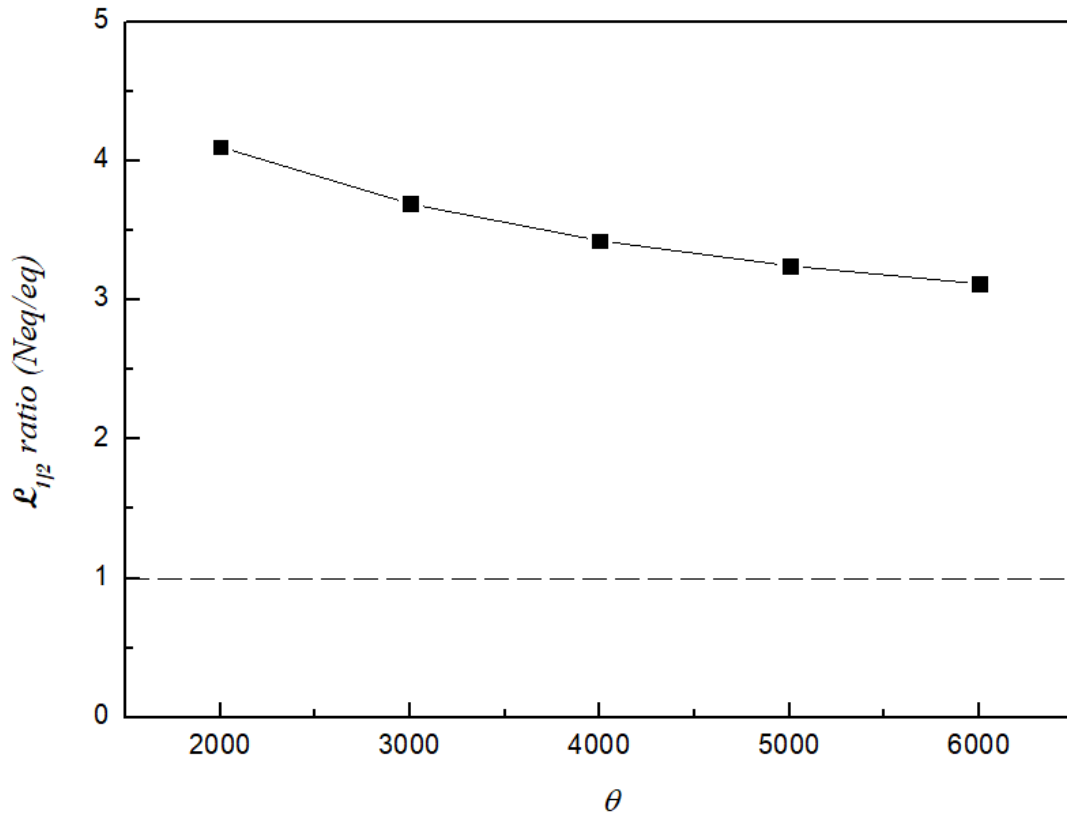


Fig. 6. Ratio of $\mathcal{L}_{1/2}$ for the nonequilibrium case to that of the equilibrium case versus θ at $E_{a,r}=50$ and $\tau^*=0.25$.

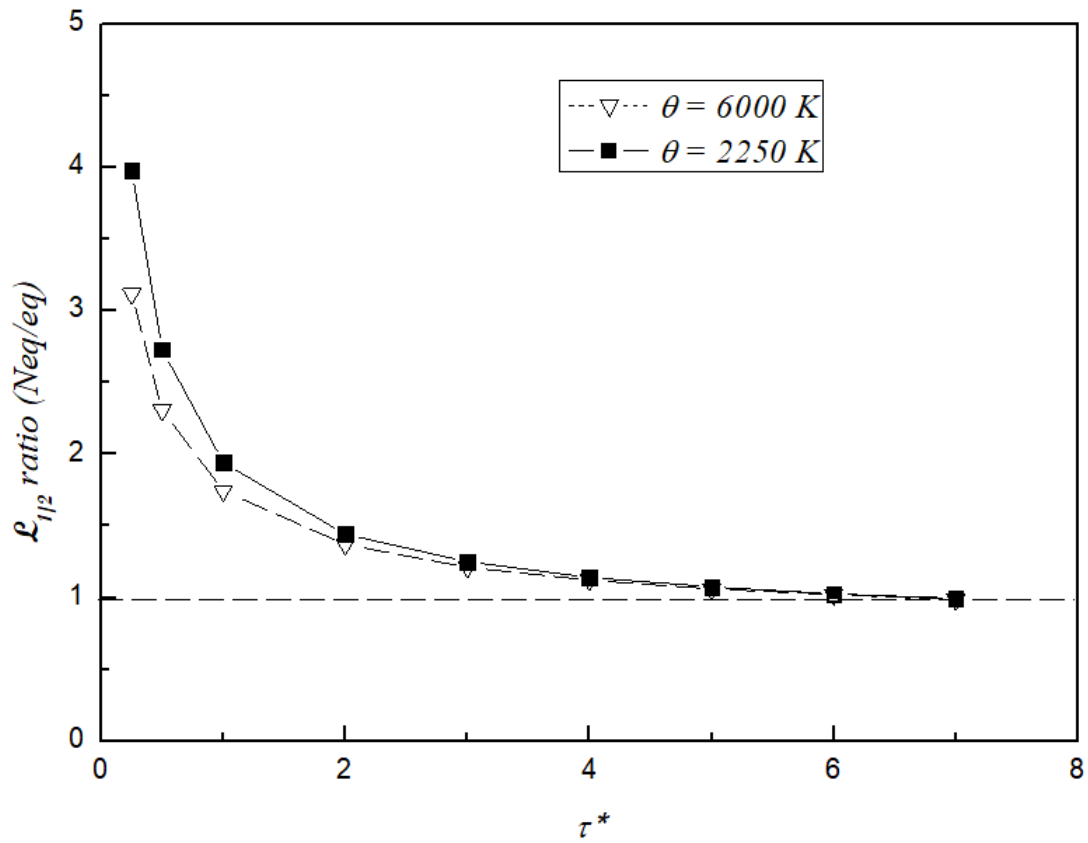


Fig. 7. Ratio of $\mathcal{L}_{1/2}$ for the nonequilibrium case to that of the equilibrium case versus τ^* at $\theta=6000$ K and at $\theta=2250$ K. $E_{a,r}=50$

3.4 Dependence on time ratio of chemical reaction time scale to vibrational relaxation time scale using two step Arrhenius model

Besides the use of the single step Arrhenius model, it is also common to use the two step model with induction zone followed by a heat-released reaction in gas detonation simulations such as hydrogen-oxygen detonation [31]. Therefore, variation on time ratio τ^* in the modified ZND model based on the temperature-dependent two step Arrhenius model were investigated while ratios of \mathcal{L}_{ind} and $\mathcal{L}_{1/2}$ were set to be 2:1 under the thermal equilibrium condition.

Fig. 8 shows the modified ZND profile in both vibrational equilibrium and nonequilibrium cases with the given parameter settings in Table 2 and the time ratio of $\tau^*=0.8$ ($\tau_c/\tau_v=0.25=\tau^*$ in Fig. 6 for the single step model case). Noted that $\tau_{1/2}$ defined in the two step model is the combination of both reaction time scale τ_c and induction time scale τ_{ind} , i.e. $\tau^* \equiv \tau_{1/2}/\tau_v = (\tau_c + \tau_{ind})/\tau_v$, compared to the case of the single step model in which $\tau^* \equiv \tau_{1/2}/\tau_v = \tau_c/\tau_v$. In the figure, an induction zone is existed right after the shock and both \mathcal{L}_{ind} ratio and $\mathcal{L}_{1/2}$ ratio are elongated by a factor of 1.9 and 2.2, respectively. Similar to the discussion in section 3.2, a range of time ratio τ^* were tested and presented in Fig. 9. It is observed that the vibrational nonequilibrium effect is significant at $\tau^* \leq 5.5$. The shortening of critical τ^* compared to the case of using the single step Arrhenius equation ($\tau^* \leq 7$) implies that the consideration of induction zone may bring a positive effect in establishing the thermal equilibrium across the profile. The $\mathcal{L}_{1/2}$ ratio of the two step model is smaller than that of the single step Arrhenius model at small τ^* . The effects of three time scales τ_{ind} , τ_c and τ_v on the change of detonation structure in two step Arrhenius model are coupled with each other and required further studies. Both the single step model and the two step model manifest the the necessity of involving the contribution of the vibrational relaxation process in the evaluation of chemical reaction rates in detonation. Direct validation of the currently proposed ZND solutions with the numerical simulations using detailed chemistry coupled with vibrational nonequilibrium effect will be conducted in the near future.

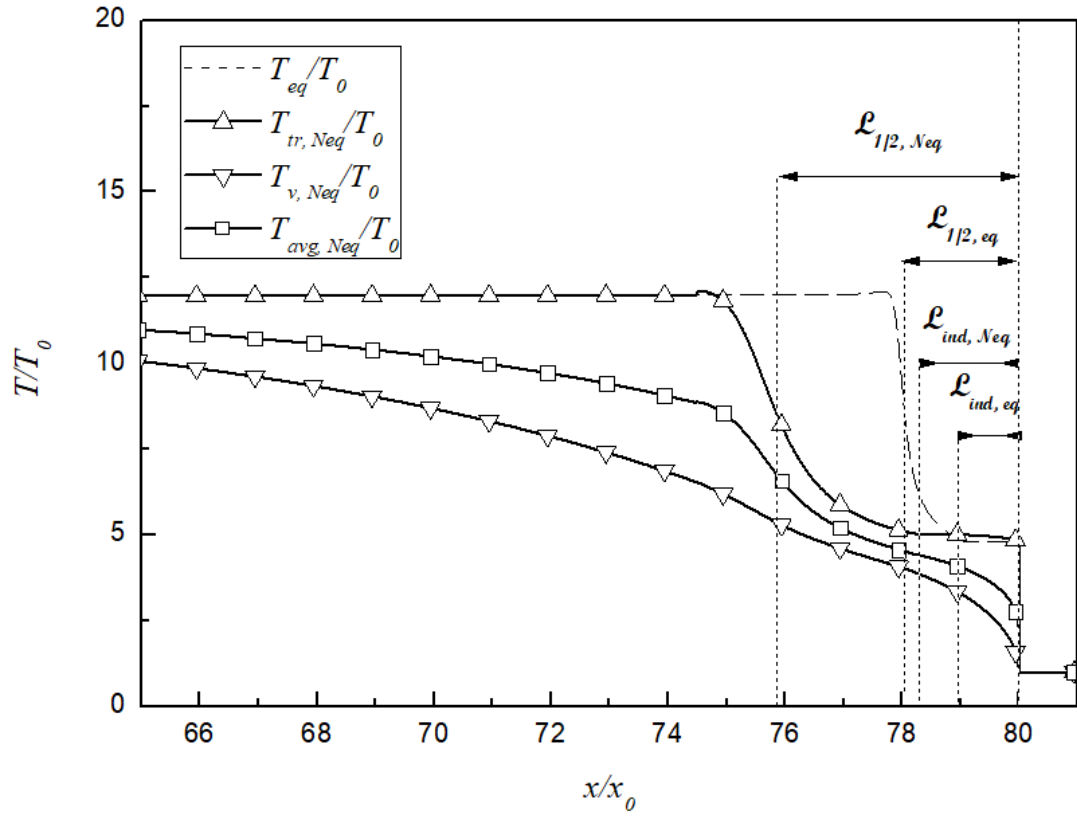


Fig. 8. Temperature ratio T/T_0 at the vibrational equilibrium state (eq) and the vibrational non-equilibrium state (Neq) using two step Arrhenius model at $\tau^*=0.8$ and $\theta=2250$ K.

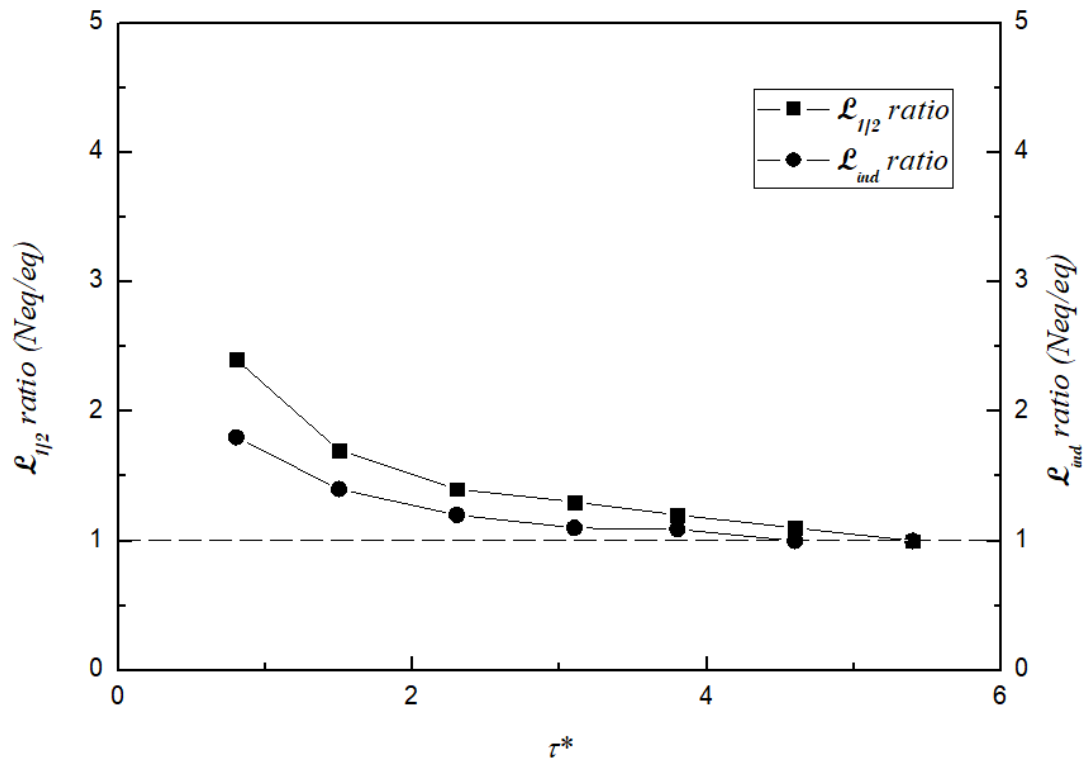


Fig. 9. Ratios of $\mathcal{L}_{1/2}$ and \mathcal{L}_{ind} for the nonequilibrium case to those of the equilibrium case versus τ^* at $E_{a,r}=50$ and $\theta=2250$ K.

4. Conclusions and Future Study

In the present study, a modified steady one-dimensional ZND model is proposed with the consideration of the vibrational nonequilibrium effect in reactant and product molecules during gas detonation. The total internal energy term in the energy conservation equation is divided into the translational-rotational mode and the vibrational mode by a ratio α across the profile. α is defined as the ratio of the translational-rotational mode of the specific heat at constant volume over the overall specific heat at constant volume while excluding the consideration of the excitation of the electrical mode in molecules. The modified ZND model formulas were derived based on the conservation laws. Both the single step and the two step Arrhenius models and the Landau Teller model were adopted as the primary descriptions for the chemical reaction and the vibrational relaxation during the detonation process, respectively. Park's two temperature model was applied in the Arrhenius models to account for the coupling between the vibrational relaxation and the chemical reaction. The model expressions are in the non-dimensional form to facilitate the parametric analysis.

The half reaction length is used to illustrate the vibrational nonequilibrium effect on gas detonation, which is defined as the distance from the shock front to where one half of the reactants is consumed from the initial state and is closely related to the detonation cell size. The induction length is considered in the two step model if the chain-initiation stage is comparable important to the reaction stage. The parametric study was conducted to compare the calculated half reaction lengths in both conventional ZND profile and the modified ZND profile. The activation energy $E_{a,r}$ in the chemical models, the time ratio τ^* of the chemical half reaction time scale to the vibrational time scale, and the characteristic vibrational temperature θ in gas detonation were examined. Results shows that the half reaction length increases with increasing $E_{a,r}$, which is due to the slow dissociation rate under the vibrational excitation. Consequently, an extra distance is required before the reaction takes place under the condition of high activation energy. In the case of large τ^* , i.e. $\tau_c \gg \tau_v$, the molecular vibrational states reach equilibrium and a reasonable agreement is found between the half reaction length of the conventional ZND model and the modified ZND solution. The importance of the vibrational nonequilibrium effect on gas detonation is demonstrated when τ_v is comparable with τ_c . Dependence on the selected θ range is less significant than $E_{a,r}$ and τ^* . With the parameter setting of $\gamma=1.2$, $Q=50$, $T_0=300$ K, $R=259.8$ J/kg K, and $E_{a,r}=50$ using single step Arrhenius model, the criteria for that the vibrational nonequilibrium effect should be considered is suggested to be

$\tau^* \leq 7$, under different θ . For the cases in which induction zone is considered with the step Arrhenius model, the criteria for that the vibrational nonequilibrium effect should be considered is suggested to be $\tau^* \leq 5.5$, under the same parameter setting in reaction model. The result implies that vibration relaxation, which starts right after the shock in the induction zone in the cases using the two step Arrhenius model, can significantly reduce $\mathcal{L}_{1/2}$ ratio compared to the case of the single step Arrhenius model at small τ^* . The critical τ^* also decreases. This criterion depends on the parameter setting in induction and reaction models.

Further investigation will be focused on the direct comparison of the currently proposed ZND solutions with the numerical simulations using detailed chemistry coupled with vibrational nonequilibrium effect. The fluid mechanics effect and the coupling between vibrational nonequilibrium and fluid dynamics will also be studied.

Acknowledgments

This work was supported by the open fund of State Key Laboratory of Explosion Science and Technology (Beijing Institute of Technology), numbered KFJJ15-09M, Natural Science Foundation of China project, numbered 11772284, and the projects of Research Grants Council, Hong Kong, under contract number CRF C5010-14E and GRF 152151/16E. The authors would also like to thank Hong Kong Innovation and Technology Commission (no. ITS/334/15FP) for financial support.

Reference

- [1] J.H. Lee, The detonation phenomenon, Cambridge University Press Cambridge, 2008.
- [2] Y.B. Zeldovich, On the theory of the propagation of detonation in gaseous systems, (1950).
- [3] J. Von Neumann, Theory of detonation waves, DTIC Document, 1942.
- [4] W. Döring, On detonation processes in gases, Ann. Phys 43 (1943) 9.
- [5] N. Tsuboi, S. Katoh, A.K. Hayashi, Three-dimensional numerical simulation for hydrogen/air detonation: Rectangular and diagonal structures, Proceedings of the Combustion Institute 29 (2002) 2783-2788.
- [6] K. Eto, N. Tsuboi, A.K. Hayashi, Numerical study on three-dimensional CJ detonation waves: detailed propagating mechanism and existence of OH radical, Proceedings of the Combustion Institute 30 (2005) 1907-1913.
- [7] B. Taylor, D. Kessler, V. Gamezo, E. Oran, Numerical simulations of hydrogen detonations with detailed chemical kinetics, Proceedings of the combustion Institute 34 (2013) 2009-2016.

- [8] B. Taylor, D. Kessler, E. Oran. Estimates of Vibrational Nonequilibrium Time Scales in Hydrogen-Air Detonation Waves. 24th International Colloquium on the Dynamics of Explosive and Reactive Systems, Taipei, Taiwan, July; 2013.
- [9] S.J. Voelkel, V. Raman, P. Varghese. Non-Equilibrium Reaction Rates in Hydrogen Combustion. 25th International Colloquium on the Dynamics of Explosions and Reactive Systems (ICDERS), Leeds, UK, August; 2015. 2-7.
- [10] H. Koo, V. Raman, P.L. Varghese, Direct numerical simulation of supersonic combustion with thermal nonequilibrium, *Proceedings of the Combustion Institute* 35 (2015) 2145-2153.
- [11] L. Shi, H. Shen, P. Zhang, D. Zhang, C. Wen, Assessment of Vibrational Non-Equilibrium Effect on Detonation Cell Size, *Combustion Science and Technology* 189 (2016) 841-853.
- [12] C.M. Tarver, Chemical energy release in the cellular structure of gaseous detonation waves, *Combustion and Flame* 46 (1982) 135-156.
- [13] C.M. Tarver, Chemical energy release in one-dimensional detonation waves in gaseous explosives, *Combustion and Flame* 46 (1982) 111-133.
- [14] C.M. Tarver, Chemical energy release in self-sustaining detonation waves in condensed explosives, *Combustion and Flame* 46 (1982) 157-176.
- [15] C.M. Tarver, Multiple Roles of Highly Vibrationally Excited Molecules in the Reaction Zones of Detonation Waves, *The Journal of Physical Chemistry A* 101 (1997) 4845-4851.
- [16] A. Gavrikov, A. Efimenko, S. Dorofeev, A model for detonation cell size prediction from chemical kinetics, *Combustion and flame* 120 (2000) 19-33.
- [17] W. Fickett, W.C. Davis, *Detonation*, University of California Press, 1979.
- [18] W.G. Vincenti, C.H. Kruger, *Introduction to physical gas dynamics*, 1965.
- [19] S. Voelkel, D. Masselot, P.L. Varghese, V. Raman, Analysis of hydrogen-air detonation waves with vibrational nonequilibrium, *AIP Conference Proceedings* 1786 (2016) 070015.
- [20] H. He, S.-T. Yu, Z.-C. Zhang. Direct calculations of one-, two-, and three-dimensional detonations by the CESE method. 43rd AIAA Aerospace Sciences Meeting and Exhibit; 2005. 229.
- [21] H. Shen, M. Parsani, The role of multidimensional instabilities in direct initiation of gaseous detonations in free space, *Journal of Fluid Mechanics* 813 (2017).
- [22] D.A. Kessler, V.N. Gamezo, E.S. Oran, Simulations of flame acceleration and deflagration-to-detonation transitions in methane-air systems, *Combustion and Flame* 157 (2010) 2063-2077.
- [23] M. Short, G.J. Sharpe, Pulsating instability of detonations with a two-step chain-branching reaction model: theory and numerics, *Combustion Theory and Modelling* 7

(2003) 401-416.

[24] J. Li, J. Ning, C.B. Kiyanda, H.D. Ng, Numerical simulations of cellular detonation diffraction in a stable gaseous mixture, *Propulsion and Power Research* 5 (2016) 177-183.

[25] C. Park, Assessment of two-temperature kinetic model for ionizing air, *Journal of Thermophysics and Heat Transfer* 3 (1989) 233-244.

[26] R.C. Millikan, D.R. White, Systematics of vibrational relaxation, *The Journal of chemical physics* 39 (1963) 3209-3213.

[27] J.J. Erpenbeck, Stability of Idealized One-Reaction Detonations, *Physics of Fluids* 7 (1964) 684.

[28] L. He, J.H. Lee, The dynamical limit of one-dimensional detonations, *Physics of Fluids* 7 (1995) 1151-1158.

[29] H. Lee, D.S. Stewart, Calculation of linear detonation instability: one-dimensional instability of plane detonation, *Journal of Fluid Mechanics* 216 (1990) 103-132.

[30] M. Short, J.J. Quirk, On the nonlinear stability and detonability limit of a detonation wave for a model three-step chain-branching reaction, *Journal of Fluid Mechanics* 339 (1997) 89-119.

[31] M. Sichel, N. Tonello, E. Oran, D. Jones. A two-step kinetics model for numerical simulation of explosions and detonations in H₂-O₂ mixtures. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*; 2002: The Royal Society. 49-82.