

Uncertainty Quantification for the Real Gas Model of Steady Planar Detonation

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1 Introduction

High-pressure conditions are employed in many combustion facilities to increase thermodynamic and fuel consumption efficiency. Detonation initiated at such conditions, like during super-knock events [1], can further increase the pressure via shock compression. The reaction processes take place near or at supercritical conditions for which ideal gas assumption does not hold. The real gas effects are related to the inter-molecular attraction, and the finite molecular volume. Complete description of real gas involves the non-ideal equation of state (EoS), thermodynamic functions, reaction kinetic law, reaction mechanism, etc [2, 3]. The real gas effect on steady planar detonation has been investigated by Astapov et al. [4] and Schmitt et al. [5] with a number of cubic EoS. The non-ideal effect increases the CJ speed by 7-12% at 10 MPa [4]. The reaction zone structure is also modified by the real gas effect [5]. However, none of these studies has attempted to quantify the uncertainty related to the full real gas model. The use of non-ideal EoS relies on the determination of molecular attraction and covolume parameters, which are related to the critical pressure and temperature in cubic EoS [6]. The determination of critical properties relies on (1) experiments, (2) group-additivity methods [6], and (3) simulation based on Lennard-Jones (L-J) potential model [7]. Experiments are essentially limited to stable and some meta-stable species, and usually has small uncertainty. Poiling et al. [6] compared the results obtained for stable species using several group contribution methods to their experimental values. The relative difference were found to less than 5% for most species. Without experimental data for the boiling point temperature, the average error of estimated critical temperature might be as high as 10%-20%. Tang et al. [2] performed a sensitivity analysis by using doubled and halved critical temperature. However, the uncertainty propagation in the combustion simulation has not been studied in great details. The present study aimed at quantifying the uncertainty induced by the molecular attraction and covolume parameters on the chemical length-scale of detonation in high-pressure H₂/air mixture. The real gas model uncertainty was also compared with that of the reaction model to evaluate their relative importance in detonation simulation.

2 Methods

We adopted the Peng-Robinson (PR) EoS to describe the state of real gas, which was proved to predict well the Chapman-Jouguet (CJ) speed at high pressure conditions [5]. The PR EoS reads

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + 2bV - b^2}, \quad (1)$$

where R is the universal gas constant; a and b are parameters to account for the inter-molecular attraction effect and the finite molecular volume effect, respectively. In PR EoS, a and b are related to the critical properties (T_c , P_c) and the acentric factor (ω) using

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \left[1 + f(\omega) \left(1 - \sqrt{T/T_c} \right) \right]^2, \quad (2a)$$

$$b = 0.07780 \frac{R T_c}{P_c}, \quad (2b)$$

$$f(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2. \quad (2c)$$

Critical properties of stable species were obtained from experiments, while the values for radicals were estimated from their molecule diameter (σ_d) and well depth (ε) [7], i.e. $T_c = 1.321\varepsilon/k_B$ and $P_c = 0.129\varepsilon/\sigma_d^3$. k_B is the Boltzman constant. The radicals were assumed to follow the L-J potential model in the correlation, therefore their acentric factors were taken as zero. For a mixture, the van der Waals mixing rules were applied for a and b [6], but the binary interaction coefficient was treated as zero. The corresponding thermodynamic functions of PR EoS have been derived by Schmitt et al. [5], which is a sum of the ideal one and the departure function. The reaction rate of the i^{th} elementary reaction in non-ideal system is described by

$$r_i = k_{f,i} \prod_{k=1}^K \left(\phi_k \frac{X_k P}{Z R T} \right)^{v'_{k,i}} - k_{r,i} \prod_{k=1}^K \left(\phi_k \frac{X_k P}{Z R T} \right)^{v''_{k,i}}. \quad (3)$$

$k_{f,i}$ and $k_{r,i}$ are the forward and reverse rate constants. Z is the compressibility factor. ϕ_k is the fugacity coefficient used to correct the reaction rate when the state departs from ideal gas assumption [2]. The forward rate constants ($k_{f,i}$) is given in the reaction mechanism. The reverse rate constant was obtained by dividing $k_{f,i}$ by the equilibrium constant. The equilibrium constant, given in Eq. (4), was derived by setting the net reaction rate as zero and the Gibbs free energy to its minimum.

$$K_{c,i} = \left(\frac{P^0}{Z R_u T} \right)^{\sum_{k=1}^K v_{k,i}} \exp \left(- \frac{\Delta G^0(T, P^0)}{R_u T} \right) \quad (4)$$

The steady planar detonation is governed by the Zel'dovich-von Neumann-Doering (ZND) model. Schmitt et al. have extended the ZND model to apply several cubic EoS [5]. In this work, the PR EoS and the corresponding thermodynamics and kinetic laws were implemented in Cantera [8]. The ZND model was numerically solved using Cantera and the Shock Detonation Toolbox [9]. The high pressure H_2/O_2 reaction mechanism from Burke et al. [10] was used for all the calculations.

In order to quantify the uncertainty propagating from a and b to the simulation results, we applied the Monte Carlo method. The uncertainty factor of a parameter in the model, denoted with ψ , was defined as

$$f = \frac{\psi^{\text{upper}}}{\psi_0} \text{ or } f = \frac{\psi_0}{\psi^{\text{lower}}}, \quad (5)$$

where ψ_0 is the nominal value, ψ^{upper} and ψ^{lower} are the upper and lower bounds. ψ was assumed to follow the log-normal distribution given in Eq. (6). f was interpreted as n_d standard deviation.

$$n_d \frac{\ln \psi / \psi_0}{\ln f} \sim \mathcal{N}(0, 1), n_d = 1, 2, 3. \quad (6)$$

The source of real gas model uncertainty depends on the method of calculating a and b for each species. The uncertainty is from experiment for stable species or from the L-J parameters for radicals. Table 1 and 2 present the critical properties and L-J parameters of all species. The uncertainty factor in table 1 was interpreted as one standard deviation. In table 2, the values given in Chemkin database

were taken as the nominal value while the calculated results were used to evaluate f . This approach is similar to the one used in the work of Zhang et al. [11]. For H atom, the well depth given by Chemkin is 2 orders of magnitude as large as the calculated results. We thus adopted an intermediate value, i.e. the calculated result using N₂ bath gas, as the nominal value. To compare the real gas model uncertainty with the reaction model uncertainty, the Monte Carlo method was also applied to the reaction rate constants. We used the temperature-dependent uncertainties provided by Nagy et al. [12], which considers the uncertainties in all Arrhenius parameters, i.e. A , n , E_a . Each parameter was assumed to follow the log-normal or normal distribution, and thus the rate constant follows a multivariate log-normal distribution [12]. In the Monte Carlo calculation, each critical property, L-J parameter or rate constant was sampled separately for 10,000 times. In addition, all critical properties and L-J parameter were sampled altogether for 20,000 times to evaluate the overall uncertainty in real gas model. An in-house Matlab program was used to sample parameters, update the mechanism file and run the ZND detonation solver.

Table 1: The nominal value (ψ_0) and uncertainty factor (f) of the critical properties of stable and meta-stable species. ($n_d = 1$)

Species	T_c		P_c		Ref.	ω	Ref.
	ψ_0/K	f	ψ_0/MPa	f			
H ₂	33.18	1.00606	1.3	1.00092	[13]	-0.217	[6]
H ₂ O	647	1.00310	22.064	1.00023	[13]	0.344	[6]
O ₂	154.58	1.00001	5.043	1.00010	[13]	0.0222	[13]
H ₂ O ₂	728	1.01393	22.0	1.04762	[14]	0.3582	[15]
N ₂	126.19	1.00008	3.3978	1.00021	[13]	0.037	[6]

Table 2: The calculated results, nominal value (ψ_0) and uncertainty factor (f) of the L-J parameters of H, O, OH, and HO₂ radicals.

Species	Bath gas	Calculated results		σ_d		ε/k_B		n_d
		$\sigma_d/\text{\AA}$	$(\varepsilon/k_B)/\text{K}$	$\psi_0/\text{\AA}$	f	ψ_0/K	f	
H ^a	He ^c	3.26	2.73	3.02	1.5	15.45	10	3
		4.16	1.69					
		4.12	1.09					
		3.76	4.09					
		3.04	14.44					
O ^b	He ^c	3.16	93.70	2.75	1.15	80.00	2.45	2
		3.00	32.69					
		2.88	71.64					
OH ^b	He ^c	3.20	151.07	2.75	1.16	80.00	1.89	2
		3.20	56.53					
		3.02	116.76					
HO ₂ ^b	He ^c	3.82	79.47	3.46	1.11	107.40	1.45	2

^a Use calculated results from Jasper et al. [16] as nominal values.

^b Use tabulated data as nominal values [17].

^c Calculated with one-dimensional-minimization approach [18].

^d Calculated with spherical average method [16].

^e Calculated with full dimensional trajectory method [16].

3 Results and Discussion

The Monte Carlo method was employed to determine the uncertainty of induction distance which was defined as the length to reach the maximum thermicity. Figure 1 presents the relative deviation of

induction distance in the Monte Carlo analysis from the nominal value in the pressure range 1-10 MPa. Only the six cases that resulted in the largest deviation were shown in the figure. These correspond to the cases when sampling (1) all critical properties and L-J parameters, (2) σ_d of HO₂, (3) P_c of H₂O₂, (4) σ_d of OH, (5) ε of HO₂ and (6) σ_d of H. Sampling all the parameters gives the largest deviation of induction distance from the nominal value, ranging from 1.1% to 15.5%. It is closed to the uncertainty caused by σ_d of HO₂, indicating that σ_d of HO₂ is the main source of uncertainty in the real gas model. P_c of H₂O₂ caused the third largest uncertainty on the induction distance, with a maximum deviation of 3%. It is thus the main source of uncertainty among all the stable or meta-stable species. Uncertainties in other parameters are not as important and induce less than 1.8% of deviation to the induction distance. Except for the case of sampling σ_d of H, the uncertainty increases linearly with pressure in Fig. 1, as the real gas effect becomes more significant at elevated pressure.

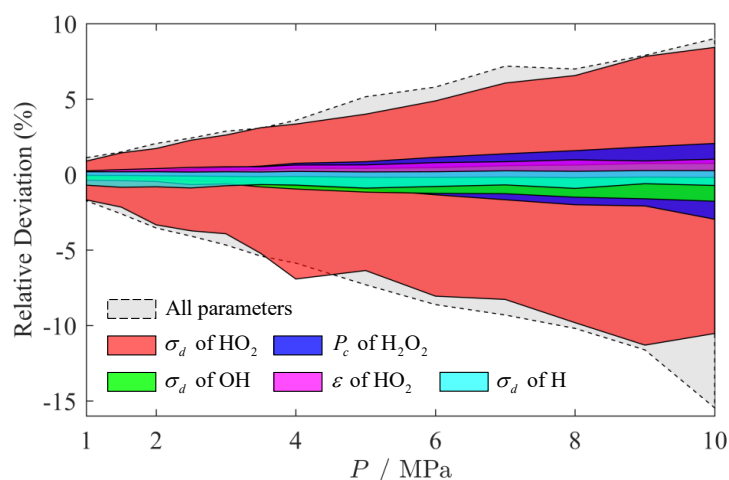


Figure 1: The relative deviation of induction distance from its nominal value when sampling (1) all parameters in the real gas model, (2) σ_d of HO₂, (3) P_c of H₂O₂, (4) σ_d of OH, (5) ε of HO₂ and (6) σ_d of H. The pressure is 1-10 MPa, the temperature is 300 K and the mixture is stoichiometric H₂/air.

It was also found that the uncertainty in the induction distance is not proportional to the uncertainty factor of critical properties or L-J parameters given in table 1 and 2. For instance, ε_d of H has an uncertainty factor of 10 but it does not affect the induction distance significantly. In addition, among the four radicals given in table 2, L-J parameters of HO₂ have the lowest uncertainty factor but they turn out to be the main source of uncertainty. In table 1, the experimental data have low uncertainty factor, but P_c of H₂O₂ results in the third largest deviation of induction distance. The uncertainty in induction distance also depends on the mole fraction and the magnitude of a and b of each species. Figure 2 presents the evolution of the molecular attraction parameter and covolume parameter with distance for all species. The parameters were weighted with their mole fraction according to the van der Waals mixing rule. Although ε_d of H has the largest uncertainty factor, $X_i a_i^{0.5}$ and $X_i b_i$ of H radical are one to two orders of magnitude smaller than the corresponding values for HO₂ and H₂O₂ in the induction zone. It indicates that the role of H in the mixing rule of a and b is minor within the induction zone. In addition, ε_d of H does not affect b_H according to the correlations of Stephan et al. [7]. As a result, the large uncertainty of ε_d of H does not cause significant impact on the induction distance. Similarly, among the four radicals considered herein, $X_i a_i^{0.5}$ and $X_i b_i$ of HO₂ are the largest in the induction zone and thus HO₂ plays a more important role in determining the simulation results. For stable or meta-stable species, the values of $X_i a_i^{0.5}$ and $X_i b_i$ are larger compared with the values for radicals, but their uncertainty factors are relatively low. As a result, HO₂ turns out to be the most important source of uncertainty in the simulation results.

The above analysis demonstrates that the determination of the a and b parameters should receive particular care when the mole fraction weighted values are large in the chemical system. This is because their contributions to the overall uncertainty tend to have a larger impact on the simulation results. When using the correlation of Stephan et al. [7], the uncertainty of σ_d is more crucial than that of ε_d . This is partly because σ_d is a cubic term while the power of ε_d is one. Our results also indicate that an order of magnitude analysis could be performed to justify neglecting a_i and b_i when their mole fraction weighted values are relatively small in the mixture. This would help to simplify the simulation and reduce computational time. Since a and b represents the molecular interaction and volume, larger or heavier molecules tend to have larger a and b . As a result, it could be possible to neglect the a and b of small species when modeling the combustion of large hydrocarbon fuels at elevated pressure.

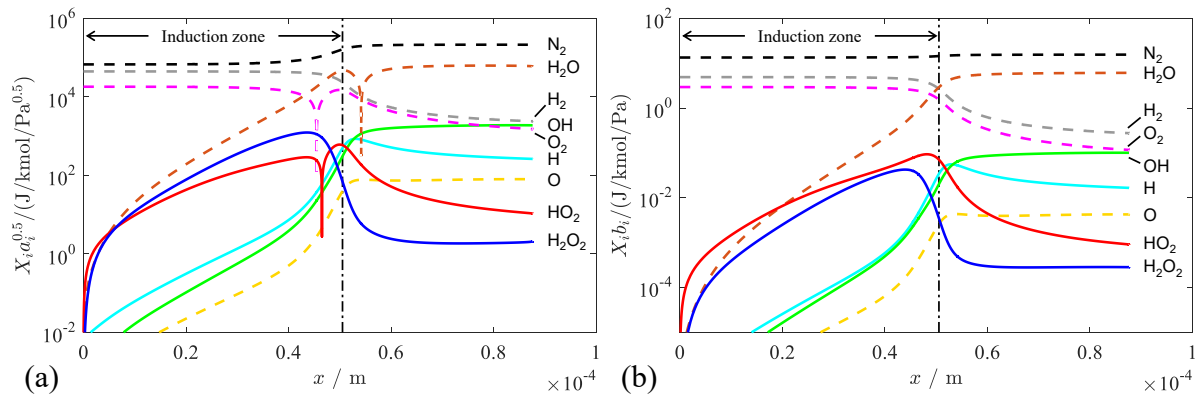


Figure 2: Evolution of (a) mole fraction weighted molecular attraction parameter ($X_i a_i^{0.5}$) and (b) mole fraction weighted covolume parameter ($X_i b_i$) with distance for different species. The mixture is a stoichiometric H_2 /air initially at the temperature of 300 K and the pressure of 5 MPa.

Reaction mechanism has been considered as the main source of uncertainty in combustion simulation. It is therefore meaningful to compare the uncertainty from the chemical kinetics with the one from the real gas model. Figure 3 presents the uncertainty caused by the real gas model and the reaction model at different initial pressures. The probability density function (PDF) of induction distance when sampling all parameters of the real gas model is presented along with the standard deviation obtained when sampling the reaction rates. Only the four reactions that brings the largest deviation were retained. In Fig. 3(a), the real gas model uncertainty increases with pressure while the reaction model uncertainty decreases with pressure. At 1 MPa, the real gas model uncertainty is almost negligible, but the standard deviation caused by R22: $H_2O_2 + H = H_2 + HO_2$ is significant; it is equal to $25.9 \mu\text{m}$. At 10 MPa, the real gas model uncertainty is smaller than the uncertainty caused by R21: $H_2O_2 (+ M) = OH + OH (+ M)$ and R22, but is close to that from R1: $H + O_2 = O + OH$. The PDF of induction distance at 10 MPa is also given in Fig. 3(b). It was found that the PDF of real gas model almost coincides with the one resulting from the rate constant of R1. The PDF induced by the rate constant of R21 and R22 spread over a much larger range. The result indicates that the real gas model uncertainty becomes comparable to the reaction model uncertainty at high pressure, but the latter still dominates the overall uncertainty of combustion simulation.

4 Conclusion

The induction distance of ZND detonation in hydrogen/air mixture was calculated at elevated pressure. The real gas effect was incorporated by using the Peng-Robinson equation of state (EoS) and its cor-

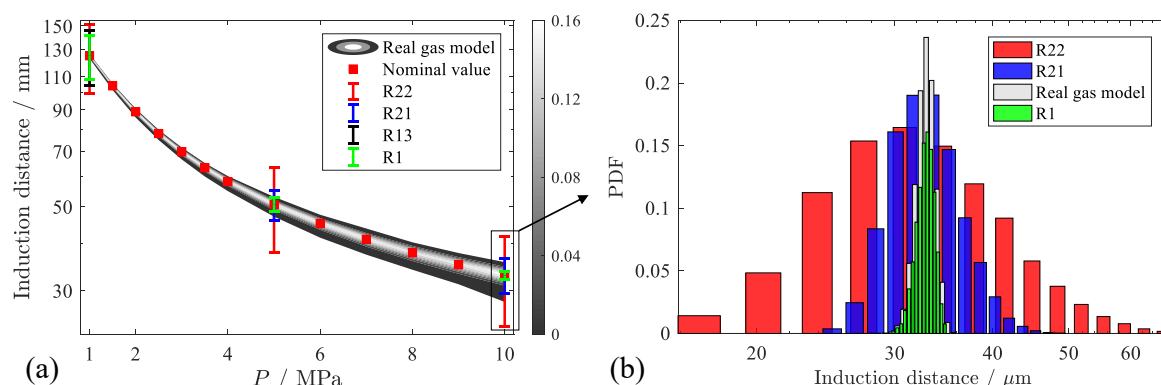


Figure 3: (a) The PDF of induction distance propagating in a stoichiometric H_2/air mixture when sampling all parameters of the real gas model and the standard deviation of induction distance when sampling the reaction rate of R1, R13, R21 and R22 at 1-10 MPa. The PDF at 10 MPa is given in (b). The temperature is fixed at 300 K. R1: $\text{H} + \text{O}_2 = \text{O} + \text{OH}$. R13: $\text{H} + \text{O}_2 (+ \text{M}) = \text{HO}_2 (+ \text{M})$. R21: $\text{H}_2\text{O}_2 (+ \text{M}) = \text{OH} + \text{OH} (+ \text{M})$. R22: $\text{H}_2\text{O}_2 + \text{H} = \text{H}_2 + \text{HO}_2$.

responding thermodynamic functions and reaction kinetic law. The uncertainty of the real gas model, originating from the molecular attraction and covolume parameters in the EoS, was quantified using a Monte Carlo sampling approach. The uncertainty increases linearly with initial pressure and is mainly determined by the species with larger mole fraction weighted molecular attraction and covolume parameters. Compared to the uncertainty caused by the reaction mechanism, the real gas model uncertainty is negligible at low pressure, but becomes on the same order of magnitude at elevated pressure. The reaction model uncertainty still dominates the overall uncertainty of combustion simulation.

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