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## Analysis of the errors associated with molecular transport parameters in combustion modeling and their effects on one-dimensional flame simulations

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**Abstract:** Recent efforts in quantifying the uncertainty of chemical kinetic mechanisms have raised important questions in the combustion community regarding acceptable agreement between models and experiments. Often, the uncertainty in transport data is either not considered or not quantified when validating kinetic mechanisms. Although different methods have been implemented in which molecular parameters are used to calculate the coefficients of diffusion, viscosity, and thermal conductivity subsequently used in chemical kinetic models, the molecular parameters themselves are subject to experimental uncertainty and thus their effects on combustion simulations should be quantified. For this initial framework, we examine decades of experiments in the literature and use Markov Chain Monte Carlo methods to estimate uncertainties on the collision diameters and well depths of molecules frequently encountered in combustion simulations. We then propagate these uncertainties through simulations of laminar methane-air flames, establishing modeling uncertainties on flame speed due to transport.

**Keywords:** *Uncertainty quantification, Lennard-Jones parameters, Flame speed*

### 1 Introduction

A chief concern in the combustion community regards the acceptable level of agreement between models and experiments, and there has been much recent discussion regarding quantifying the uncertainty in combustion models [1]. As the sizes of chemical kinetic mechanisms increase, particularly in the case of higher carbon-number fuels, many more unknowns are introduced into the combustion models because reaction rates with these species have not been investigated as thoroughly as smaller fuels. Various efforts have recently been made to both quantify the uncertainty in chemical mechanisms and unify the community in this effort [2, 3, 4]. These include uncertainty propagation investigations in correlations among Arrhenius parameters in ignition times [5] as well as uncertainty propagation in flame structure and speed [6, 7].

However, uncertainty in transport is often not investigated or accounted for in flame models, despite that the sensitivities to transport parameters can be on the same order of magnitude as reaction rates [8]. Most recent efforts regarding uncertainty in transport have focused on sensitivity analyses of diffusion coefficients in flames with Lewis numbers that deviate significantly from unity [9, 10], with uncertainty propagation applied to flame extinction [11, 12], although some studies have specifically investigated the sensitivities of the more fundamental molecular transport parameters,

such as collision diameter  $\sigma$ , well depth  $\epsilon$ , dipole moment  $\mu$ , and polarizability  $\alpha$ , among others [8]. Diffusion coefficients  $D$ , like the coefficients of conductivity  $\lambda$  and viscosity  $\eta$ , are calculated from these molecular parameters in various transport packages such as TRANFIT [13] for CHEMKIN-II [14]. The relationship between these molecular parameters and high-level combustion model outputs is depicted in Figure 1, and a good review of current calculation methods is given by Brown et al. [15]. Transport codes that calculate these transport coefficients from molecular parameters

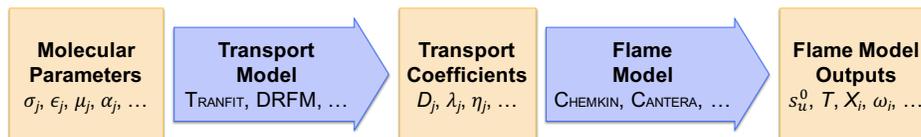


Figure 1: Role of molecular transport parameters in the present discussion. Not depicted: roles of chemical mechanism and simulation conditions such as inlet temperature, pressure, mixture, etc.

are subject to change, however. In particular, some transport models have been found to poorly predict the transport coefficients from the molecular parameters in certain regimes, and alternatives have been proposed [16]. Thus, regardless of the model in use, the underlying uncertainty in the molecular parameters must be quantified, so that the uncertainty in the transport coefficients can be quantified, so that the uncertainty in the high-level combustion model can be quantified. In this paper we initiate a framework through which more refined calculations can be made as we collect more data on molecular transport parameters.

## 2 Method

Molecular transport parameters such as collision diameter  $\sigma$  and well depth  $\epsilon$  are used in models to describe the intermolecular interactions between molecules [17]. Unfortunately, few “direct” methods exist to determine these interactions, with the most direct methods being molecular beam scattering, and—if the well depth is deep enough—spectroscopy [18]. Statistical mechanics gives a relationship between the parameters and the second coefficient of the virial equation of state, which can be experimentally measured [18, 19, 20]. Likewise, kinetic theory gives a relationship between the parameters and each of the coefficients of diffusion, viscosity, and thermal conductivity [17, 18]. Although viscosity measurements are considered the most dependable due to their relatively small experimental uncertainty [18], measurements prior to 1970 are considered unreliable due to catalyzing reactions in the experimental apparatus at high temperatures [15, 18]. In the interest of conserving space, we restrict this paper to uncertainties associated with virial coefficient measurements, for which a thorough compilation of experimental data is available spanning the years 1907–1979 [21], but we build a framework such that other data may be readily included.

First, we must determine the uncertainty in molecular transport parameters. For each experiment type that records a measurable quantity  $\mathcal{M}_{j,exp}$  for molecular species  $j$ , a relationship exists for predicting  $\mathcal{M}_j$  as a function of  $\sigma_j$ ,  $\epsilon_j$ , and other molecular parameters (indexed by  $i$ ) that we collectively refer to as  $\mathcal{X}_{i,j}$ . Thus,  $\mathcal{M}_{j,pred}(\mathcal{X}_{i,j}, \dots)$ , where  $\dots$  indicates the influence of other variables in the experiment, such as temperature  $T$  or pressure  $p$ . For each experiment measuring  $\mathcal{M}_{j,exp}$ , there is an associated uncertainty  $\Delta\mathcal{M}_{j,exp}$ . For this paper,  $\mathcal{M}_j$  is the second coefficient of the virial equation of state,  $B_2$ . For a Lennard-Jones fluid,  $B_2$  can be calculated using the

closed-form expression in Equation 1 [20]:

$$\mathcal{M}_{j,pred}(\mathcal{X}_{i,j}, \dots) = B_2(T, \sigma, \epsilon) = \frac{2}{3}\pi\sigma^3\sqrt{2\pi}\left(\frac{\epsilon}{k_B T}\right)^{1/4} H_{\frac{1}{2}}\left(-\sqrt{\frac{\epsilon}{k_B T}}\right) \quad (1)$$

where  $H_n$  is a Hermite function of fractional order  $n = \frac{1}{2}$  and  $k_B$  is the Boltzmann constant. Though technically derived for monatomic species, this and similar expressions have been shown to reproduce the data of polyatomic molecules reasonably well [18]. For each species  $j$ , a joint posterior PDF of  $\mathcal{X}_{i,j}$  in Equation 1 is generated using a Bayesian inference procedure to compare  $\mathcal{M}_{j,pred}(\mathcal{X}_{i,j}, \dots)$  to available  $\mathcal{M}_{j,exp} \pm \Delta\mathcal{M}_{j,exp}$ . Experimental uncertainties are interpreted as one standard deviation in an additive Gaussian error model. The inference is conducted using a Markov Chain Monte Carlo technique (MCMC) employing adaptive Metropolis sampling [22]. The MCMC chain is run for 50,000 samples with 50,000 samples for burn-in. The peak of this joint posterior PDF yields  $\sigma_{j,opt}$  and  $\epsilon_{j,opt}$ . Since  $\sigma_j$  and  $\epsilon_j$  are highly correlated, using conditional PDFs to obtain independent  $\Delta\sigma_j$  and  $\Delta\epsilon_j$  ranges is not appropriate [22]. Instead, we randomly sample 30 combinations of  $\sigma_j$  and  $\epsilon_j$  from the posterior PDF of each molecule.

We run 1-D flame simulations for a range of  $\phi$  using  $\sigma_{j,opt}$  and  $\epsilon_{j,opt}$  for all species investigated using the CHEMKIN-II [14] application PREMIX [23] with mixture-averaged and multicomponent transport. Then, for a single species  $j$ , we use the 30 samples to change  $\sigma_j$  and  $\epsilon_j$  while holding the properties of the other species constant, and rerun the simulations for the same range of  $\phi$ . We estimate the associated uncertainty in unburned flame speed,  $\Delta s_{u,j}^0$ , by equating it to the overall range of  $s_{u,j}^0$  reported by all the simulations for a given  $\phi$ . Finally, we sum the  $\Delta s_{u,j}^0$  values in quadrature for all species to get the total uncertainty in flame speed,  $\Delta s_{u,tot}^0$ . This approach assumes that the uncertainties due to each species are independent of one another [24].

In this paper, we only consider the uncertainties for the molecules  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{CO}$ . For molecules with permanent dipoles and very small molecules like  $\text{CO}$  and  $\text{H}_2$ , Equation 1 would normally have correction terms to account for a Stockmayer potential and quantum effects, respectively [18]. To save space, we do not consider these corrections in this paper but will do so in future studies. Furthermore, we only consider  $\text{CH}_4$ -air flames at standard conditions ( $P_{in} = 1$  atm,  $T_{in} = 300$  K), spanning the range of  $\phi$  corresponding to the flammability limits. For the results presented in this paper, this procedure corresponds to 3,264 PREMIX simulations.

### 3 Results

The results of the experimental data analysis to determine the uncertainty in molecular parameters are listed in Table 1. The joint PDFs of  $\sigma_j$  and  $\epsilon_j$  are shown in Figure 2. Note that  $\sigma_j$  and  $\epsilon_j$  are

Table 1: Summary of optimized molecular transport parameters with suggested bounds.

| Species       | $\sigma_{min}$ [Å] | $\sigma_{opt}$ [Å] | $\sigma_{max}$ [Å] | $\epsilon_{min}$ [K] | $\epsilon_{opt}$ [K] | $\epsilon_{max}$ [K] |
|---------------|--------------------|--------------------|--------------------|----------------------|----------------------|----------------------|
| $\text{CH}_4$ | 3.884              | <b>3.892</b>       | 3.899              | 145.2                | <b>145.6</b>         | 146.1                |
| $\text{O}_2$  | 3.527              | <b>3.548</b>       | 3.561              | 115.4                | <b>116.0</b>         | 116.9                |
| $\text{N}_2$  | 3.720              | <b>3.731</b>       | 3.741              | 95.23                | <b>95.44</b>         | 95.64                |
| $\text{H}_2$  | 2.863              | <b>2.889</b>       | 2.912              | 29.80                | <b>30.19</b>         | 30.62                |
| $\text{CO}$   | 3.764              | <b>3.837</b>       | 3.902              | 99.61                | <b>100.7</b>         | 101.9                |

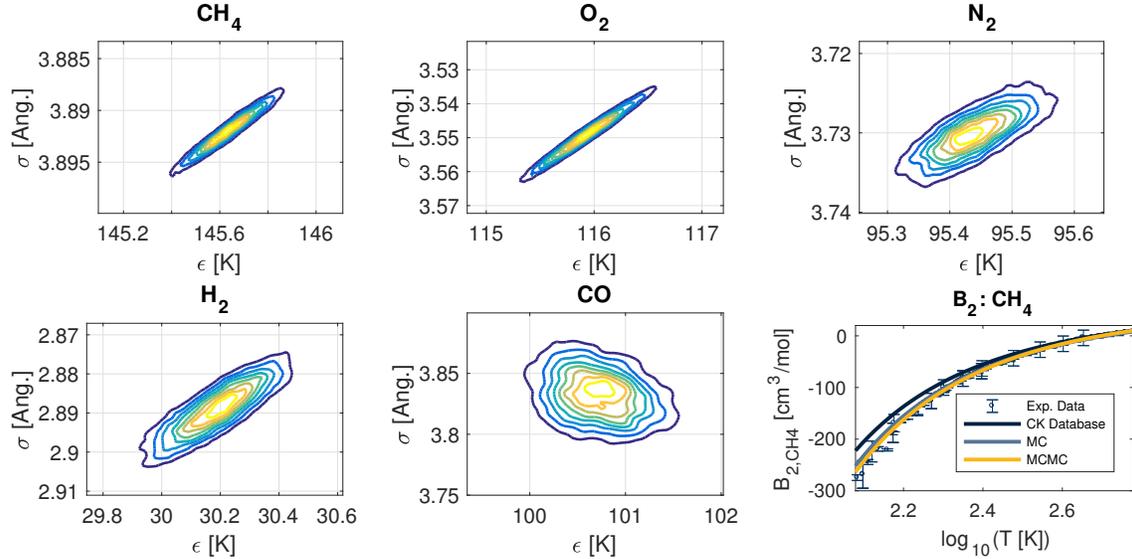


Figure 2: Contour plots of MCMC results for the different molecules (top row left to right, bottom row left to center), comparison of Equation 1 with experimental data [21] for  $\text{CH}_4$  (bottom row right)

highly correlated for most of the species. This has been discussed in the literature [15, 19] and will not be elaborated upon here in the interest of space. For illustrative purposes, the bottom right of Figure 2 shows a comparison of experimental data for  $B_{2,\text{CH}_4}$  with Equation 1 is shown in the bottom right of Figure 2 using both our MCMC-optimized parameters for  $\text{CH}_4$  and the parameters in the original CHEMKIN database. We also show results from a less sophisticated Monte Carlo (MC) method, but do not discuss this here. In this example for  $\text{CH}_4$ , the MCMC-optimized parameters better reproduce the low temperature data than those in the original CHEMKIN database.

The PREMIX flame speed results are summarized in Table 2, and visually displayed in the left of Figure 3. In the right of Figure 3, the relative uncertainty associated with  $\Delta s_u^0$  for each individual species is plotted as a function of  $\phi$ . Overall, values of  $s_u^0$  using our optimized transport parameters from Table 1 are lower than those using the transport parameters in the original CHEMKIN database. Furthermore, those unmodified results fall outside the  $\Delta s_u^0$  we have reported for most  $\phi$  we examined. As seen in Table 2, large absolute uncertainties occur more frequently for rich values of  $\phi$ . The largest source of uncertainty is due to the species  $\text{N}_2$  and  $\text{O}_2$ , which make up most of the gas mixture. In general, incorporating the uncertainty in transport parameters results in greater  $\Delta s_u^0$  for multicomponent transport simulations than for mixture-averaged ones.

Table 2: Influence of the parameters of each species on multicomponent  $s_u^0$  for different  $\phi$  in [cm/s].

| $\phi$ | $s_u^0$ | $\Delta s_{u,tot}^0$ | $\Delta s_{u,\text{CH}_4}^0$ | $\Delta s_{u,\text{O}_2}^0$ | $\Delta s_{u,\text{N}_2}^0$ | $\Delta s_{u,\text{H}_2}^0$ | $\Delta s_{u,\text{CO}}^0$ |
|--------|---------|----------------------|------------------------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|
| 0.60   | 11.28   | 0.02                 | 0.00                         | 0.00                        | 0.02                        | 0.00                        | 0.01                       |
| 0.80   | 27.19   | 0.04                 | 0.00                         | 0.01                        | 0.04                        | 0.01                        | 0.01                       |
| 0.90   | 34.32   | 0.06                 | 0.00                         | 0.01                        | 0.06                        | 0.01                        | 0.00                       |
| 1.00   | 38.76   | 0.07                 | 0.01                         | 0.02                        | 0.06                        | 0.01                        | 0.00                       |
| 1.20   | 35.74   | 0.08                 | 0.01                         | 0.06                        | 0.05                        | 0.01                        | 0.01                       |
| 1.40   | 15.21   | 0.05                 | 0.01                         | 0.04                        | 0.03                        | 0.01                        | 0.00                       |
| 1.60   | 8.54    | 0.03                 | 0.02                         | 0.02                        | 0.01                        | 0.02                        | 0.00                       |

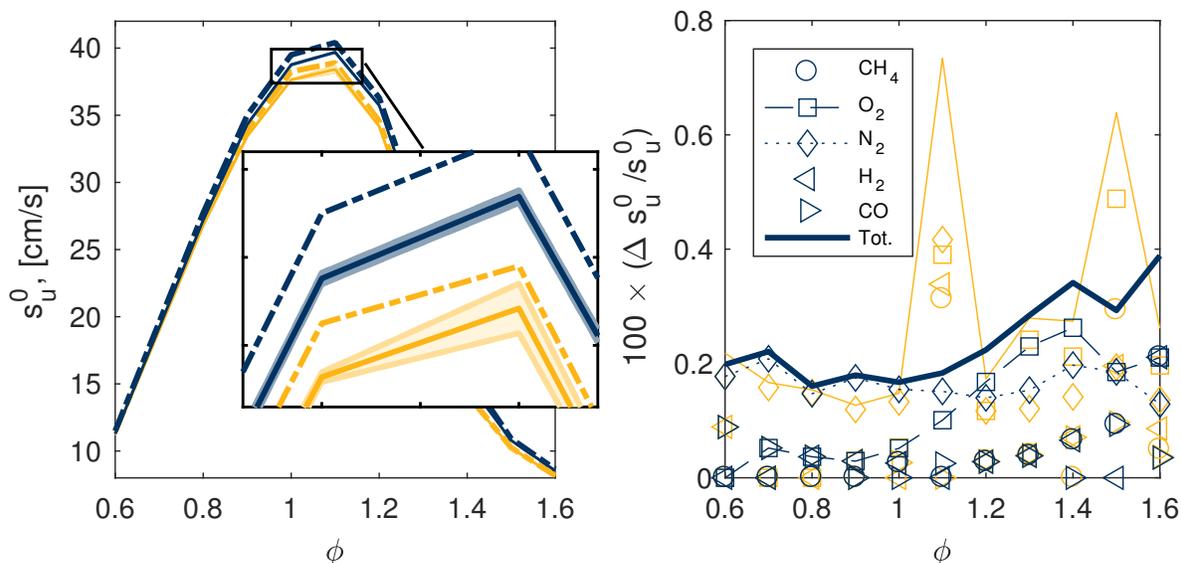


Figure 3: Calculated  $s_u^0$  using MCMC-optimized values in Table 1 (—) with  $\Delta s_{u,tot}^0$  depicted using shaded regions, calculated  $s_u^0$  using the parameters in the original CHEMKIN database (- - -) (left), relative uncertainty for each species (right). Multicomponent results in blue, mixture-averaged results in yellow.

#### 4 Discussion and conclusion

In this paper, we built a framework for incorporating the uncertainty associated with species transport parameters into flame simulations. Joint PDFs of the molecular transport parameters of CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub> and CO were obtained from uncertainty in experimental virial coefficient data using a Markov Chain Monte Carlo-based method. Incorporating the uncertainties into PREMIX simulations of CH<sub>4</sub>-air flames at standard conditions introduce relative uncertainties of up to 0.7% in flame speed. These uncertainties are generally larger for multicomponent transport simulations and richer  $\phi$ . O<sub>2</sub> is a deficient species in rich flames and so its uncertainty plays a larger role. For example, the chain-branching reaction  $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$  has been shown to contribute more to the evaluation of flame speed for rich H<sub>2</sub>-O<sub>2</sub> flames than in both stoichiometric and lean H<sub>2</sub>-O<sub>2</sub> flames at 1 atm [11]. Without reducing the uncertainty of the transport parameters of these molecules, chemical mechanisms for CH<sub>4</sub>-air cannot be expected to discern differences smaller than what we show here at standard conditions. Thus, previous studies performed by our research group reporting relative errors of 0.25% [25] in flame speed from transport changes must be interpreted cautiously. Future investigations with our framework will incorporate both more species and more types of data from which transport parameters can be discerned, such as viscosity measurements. We will also examine more fuels and more flame conditions, particularly at higher pressures, where  $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$  remains important.

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## References

- [1] Alison S. Tomlin. *Proc. Combust. Inst.*, 34 (2013) 159–176.
- [2] Michael Frenklach. *Proc. Combust. Inst.*, 31 I (2007) 125–140.
- [3] Trent Russi, Andrew Packard, Ryan Feeley, and Michael Frenklach. *J. Phys. Chem. A*, 112 (2008) 2579–2588.
- [4] T. Turányi, T. Nagy, I. Gy. Zsély, M. Cserhádi, T. Varga, B. T. Szabó, I. Sedyó, P. T. Kiss, A. Zempléni, and H. J. Curran. *Int. J. Chem. Kinet.*, 44 (2012) 284–302.
- [5] Jens Prager, Habib N. Najm, Khachik Sargsyan, Cosmin Safta, and William J. Pitz. *Combust. Flame*, 160 (2013) 1583–1593.
- [6] M. T. Reagan, H. N. Najm, P. P. Pébay, O. M. Knio, and R. G. Ghanem. *Int. J. Chem. Kinet.*, 37 (2005) 368–382.
- [7] David A. Sheen, Xiaoqing You, Hai Wang, and Terese Løvås. *Proc. Combust. Inst.*, 32 (2009) 535–542.
- [8] Nancy J. Brown and Kenneth L. Revzan. *Int. J. Chem. Kinet.*, 37 (2005) 538–553.
- [9] Manoj K. Mishra, Richard Yetter, Yakir Reuven, Herschel Rabitz, and Mitchell D. Smooke. *Int. J. Chem. Kinet.*, 26 (1994) 437–453.
- [10] Yufei Dong, Adam T. Holley, Mustafa G. Andac, Fokion N. Egolfopoulos, Scott G. Davis, Prankul Middha, and Hai Wang. *Combust. Flame*, 142 (2005) 374–387.
- [11] G. Esposito and H. K. Chelliah. *Combust. Flame*, 159 (2012) 3522–3529.
- [12] G. Esposito, B. G. Sarnacki, and H. K. Chelliah. *Combust. Theory Model.*, 16 (2012) 1029–1052.
- [13] R. J. Kee, G. Dixon-Lewis, J. Warnatz, M. E. Coltrin, and J. A. Miller. A Fortran Computer Code Package for the Evaluation of Gas-Phase Multicomponent Transport Properties. Technical Report SAND86-8246, Sandia National Laboratories, Livermore, CA, USA, 1986.
- [14] Robert J. Kee, Fran M. Rupley, and J. A. Miller. CHEMKIN II: A FORTRAN Chemical Kinetics Package for the Analysis of Gas-phase Chemical Kinetics. Technical Report SAND-89-8009B, Sandia National Laboratories, Livermore, CA, USA, 1992.
- [15] Nancy J. Brown, Lucas A.J. Bastien, and Phillip N. Price. *Prog. Energy Combust. Sci.*, 37 (2011) 565–582.
- [16] P. Paul and J. Warnatz. *Symp. Combust.*, 27 (1998) 495–504.
- [17] Joseph O. Hirschfelder, Charles F. Curtiss, and R. Byron Bird. *Molecular Theory of Gases and Liquids*. John Wiley & Sons, Inc., New York, 2nd edition, 1964.
- [18] Geoffrey C. Maitland, Maurice Rigby, E. Brian Smith, and William A. Wakeham. *Intermolecular Forces: Their Origin and Determination*. Oxford University Press, Oxford, UK, 1981.
- [19] E. A. Mason and T. H. Spurling. *The Virial Equation of State*. Pergamon Press, Oxford, UK, 1969.
- [20] Brian Cowan. Non-Ideal Gases. In *Top. Stat. Mech.*, chapter 3. Imperial College Press, London, 2005.
- [21] J.H. Dymond and E. Brian Smith. *The Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation*. Oxford University Press, New York, NY, 1980.
- [22] Stefano Andreon and Brian Weaver. *Bayesian Methods for The Physical Sciences*. 2015.
- [23] Robert J. Kee, James Miller, Mitchell D. Smooke, and Joseph F. Grcar. PREMIX: a Fortran program for modeling steady laminar one-dimensional premixed flames. Technical Report SAND85-8240, Sandia National Laboratories, Livermore, CA, USA, 1985.
- [24] Hugh W. Coleman and W. Glenn Steele. *Experimentation, Validation, and Uncertainty Analysis for Engineers*. John Wiley & Sons, Inc., Hoboken, NJ, USA, 3rd edition, 2009.
- [25] Daniel I Pineda and Jyh-Yuan Chen. Effects of updated transport properties of singlet oxygen species on steady laminar flame simulations. In *2016 Spring Tech. Meet. West. States Sect. Combust. Inst.*, number Paper 1B01, Seattle, WA, 2016. University of Washington, The Combustion Institute.