

Western States Section of the Combustion Institute - Fall 2017 Meeting
Hosted by the University of Wyoming
October 2-3, 2017.

Uncertainty of transport parameters in flame models: a database from virial coefficient measurements

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In combustion models, the uncertainty in transport data is often either not considered or not quantified when validating chemical kinetic mechanisms. The molecular parameters used to determine the coefficients of diffusivity, viscosity, and thermal conductivity are subject to experimental uncertainty and thus can influence model predictions. In this study, we build on previous efforts establishing a framework for quantifying the uncertainty in flame models due to transport. We examine decades of experimental data on the coefficients of the virial equation of state for several key combustion molecules, and use Markov Chain Monte Carlo methods to generate a distribution of possible fits consistent with the data. With these distributions, we establish a new publicly-available transport database and combine it with a relatively untuned mechanism in the literature, propagating the distributions through transport models and flame models to obtain uncertainties on species diffusivities and flame speed. Results show significant differences from established parameter values for some species, and that the uncertainty in flame behavior from transport uncertainty is largely governed by the species that dominate the fresh gas mixture, along with species involved in rate-limiting reactions. This work establishes a protocol for future comparison with experimental flame data.

1 Introduction

Concerns have been raised in the community regarding uncertainty in combustion models [1], and many efforts have been made to quantify the uncertainty in chemical kinetic mechanisms [2, 3, 4]. Notable examples with specific regard to chemistry include investigations in correlations among Arrhenius parameters in ignition [5, 6] and in flame structure and speed [7, 8].

Although the uncertainty in chemistry is large (especially for large fuels), sensitivities to transport parameters can be on the same order of magnitude as reaction rates [9]. Researchers have investigated sensitivity analyses of diffusion coefficients in flames with significantly off-unity Lewis numbers [10, 11] and in flame extinction [12, 13]. Most relevant to this work, some studies have investigated the sensitivities of molecular transport parameters (i.e. collision diameter σ , well depth ϵ , dipole moment μ , and polarizability α , etc) [14, 9]. Macroscale transport coefficients such as diffusivity D , conductivity λ , and viscosity η are calculated from these molecular parameters in the transport models of various combustion simulation codes, using either empirical fits or kinetic theory to do so [15]. The uncertainties in these macroscale coefficients influence the uncertainty of flame models, and so the underlying uncertainties in the molecular transport parameters must be

quantified. Expanding on previous research [16], this paper aims to provide the combustion community with an active and accessible database of the best estimates and uncertainties of molecular transport parameters.

2 Methods

2.1 Molecular interaction model and Markov Chain Monte Carlo procedure

To quantify the uncertainties in flame models due to transport, the uncertainties in the transport must first be quantified. Molecular transport parameters such as collision diameter (σ) and well depth (ϵ) are used in models that describe the binary intermolecular interactions between molecules [17]. The uncertainties in these parameters stem from the uncertainties in the experiments used to determine them. For relatively stable species, various experimental methods exist to measure macroscale properties of these molecular species (viscosity, diffusivity, the second coefficient of the virial equation of state, etc.) and subsequently infer the molecular parameters from statistical mechanical or kinetic theory expressions for the measured macroscale quantities [18]. Viscosity data is often considered the most reliable [19], but many measurements from prior to 1970 are considered unreliable due to the suspected presence of catalyzing reactions in the experimental measurement apparatus at high temperatures [15, 18]. As in our initial study [16], we continue to determine the best estimates and uncertainties of molecular transport parameters based on virial coefficient measurements, for which thorough compilations of experimental data are available spanning the years 1897-1998 [20, 21].

For each experiment that measures the second coefficient of the virial equation of state $B_{2,j,exp}(T)$ for molecular species j , a relationship exists that models $B_{2,j}(T)$ as a function of σ_j , ϵ_j , and other molecular parameters, though we don't consider those in this study. Thus, $B_{2,j,model}(T, \sigma_j, \epsilon_j)$ attempts to replicate $B_{2,j,exp}(T)$ via best-estimates for σ_j and ϵ_j . The expression for $B_{2,j,model}(T, \sigma_j, \epsilon_j)$ we use in this study is given in Equation 1 [22]:

$$B_{2,j,model}(T, \sigma_j, \epsilon_j) = -2\pi \int_0^{\infty} r^2 [e^{-U(r)/k_B T} - 1] dr \quad (1)$$

where, for a Lennard-Jones fluid, $U(r)$ is given by Equation 2:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

Though technically derived for non-polar monatomic species, this and similar expressions have been shown to reasonably reproduce the data of polyatomic [18] and slightly polar [19] molecules.

For each experiment measuring $B_{2,j,exp}(T)$, there is an associated uncertainty $\Delta B_{2,j,exp}(T)$. Because of this, there is an uncertainty in $B_{2,j,model}(T, \sigma_j, \epsilon_j)$, ultimately corresponding to the uncertainties $\Delta\sigma_j$ and $\Delta\epsilon_j$. As in our previous study, for each species j , a joint posterior PDF of (σ_j, ϵ_j) in Equation 1 is generated using a Bayesian inference procedure comparing $B_{2,j,model}(T, \sigma_j, \epsilon_j)$ to all available $B_{2,j,exp}(T) \pm \Delta B_{2,j,exp}(T)$. Experimental uncertainties are interpreted as one standard deviation in an additive Gaussian error model. The inference is conducted using a Markov Chain Monte Carlo (MCMC) technique employing adaptive Metropolis sampling [23]. The MCMC chain

is run for 50,000 samples with 50,000 samples for burn-in. A multivariate normal distribution is fitted to the resulting joint posterior PDF for each molecule j , with a peak corresponding to $\sigma_{j,opt} = \sigma_{j,mean}$ and $\epsilon_{j,opt} = \epsilon_{j,mean}$. We randomly sample 30 combinations of σ_j and ϵ_j from this multivariate normal distribution for subsequent use in flame simulations. Other parameters, such as permanent dipole moment μ_j , polarizability α_j , and rotational relaxation $Z_{rot,j}$ are much less influential in flame models [9] than σ_j and ϵ_j and are not considered here.

2.2 Flame simulations

We run 1-D adiabatic free flame simulations for a range of ϕ using $\sigma_{j,opt}$ and $\epsilon_{j,opt}$ for all species investigated using CANTERA [24] with multicomponent transport and the Soret effect enabled. In many cases, $\sigma_{j,opt}$ and $\epsilon_{j,opt}$ deviate significantly from the values reported in the original CHEMKIN database [25]. Thus, to reduce the influence of biases associated with chemical kinetic mechanisms that have been tuned (with potentially inaccurate transport data) to match flame experiments, we use a relatively “un-tuned” mechanism in the literature [26] for CH₄-air combustion. For a single species j , we use the 30 aforementioned samples to change σ_j and ϵ_j while holding the properties of the other species constant, and re-run the simulations for the same range of ϕ . 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 of the simulations for a given ϕ . 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 [27]. We use this same approach to determine the self-diffusion coefficients D_{jj} of the selected species j at flame temperatures.

In this paper, we only consider the uncertainties for the molecules CH₄, O₂, N₂, H₂, CO, Ar, CO₂, C₂H₆, C₂H₂, and C₂H₄. These are molecules that are simultaneously in the mechanism we use [26] and for which experimental virial coefficient data exist [20, 21]. For the significant but unstable species H, H₂O₂, HO₂, O, and OH—for which no experimental virial coefficient data exist—the transport parameter values recommended by Paul et al. [14, 28] are assumed. These values have been shown [15] to better reproduce some experimental diffusivity data in the literature than those in the original CHEMKIN database. The transport properties of all other species are unchanged from that original database, however.

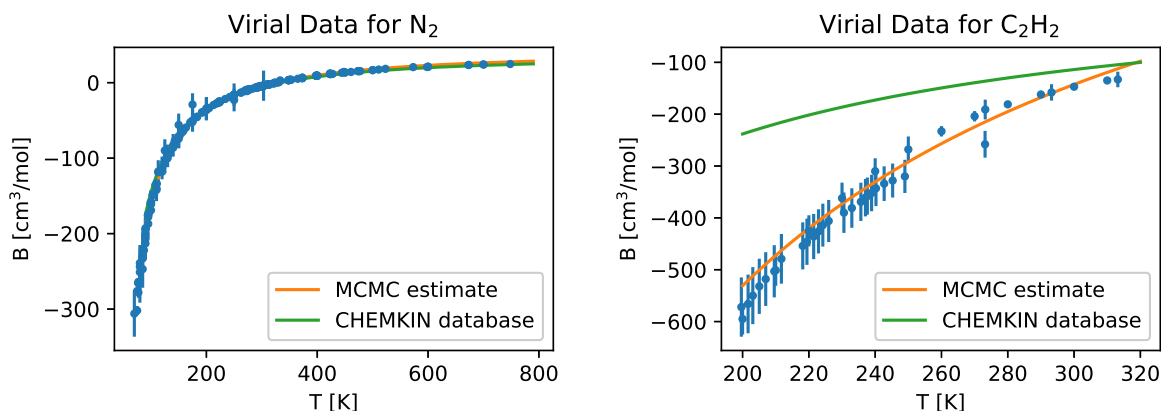
3 Results and Discussion

3.1 Optimized molecular transport parameters and virial coefficient data agreement

The results of the MCMC optimization procedure, including the optimized molecular transport parameters and their corresponding variances and covariances, are listed in Table 1. For some species, the optimized values are significantly different from those listed in the original CHEMKIN database; the optimized parameters often show much better agreement with the experimental virial coefficient data, and some notable examples are shown in Figure 1. While the values for some well-known species, such as N₂, are in good agreement, others, such as C₂H₂, are far off. Similar plots of the agreements with experiment for all of the species in Table 1 are available in our online GitHub repository [29], along with all of the original experimental data points and uncertainties

Table 1: Summary of optimized molecular transport parameters with covariance parameters.

Species	σ_{opt} [Å]	ϵ_{opt} [K]	var_{σ} [Å ²]	var_{ϵ} [K ²]	$\text{covar}_{\sigma\epsilon}$ [Å K]
CH ₄	3.861	146.2	9.726E-7	1.980E-3	-4.273E-5
O ₂	3.523	117.2	1.421E-5	2.968E-2	-6.298E-4
N ₂	3.769	95.34	1.423E-6	9.254E-4	-2.542E-5
H ₂	2.898	30.63	3.515E-5	1.432E-2	-5.455E-4
CO	3.791	99.99	4.213E-5	4.583E-2	-1.259E-3
Ar	3.462	118.7	1.463E-6	4.456E-3	-7.815E-5
CO ₂	4.316	200.2	9.890E-7	2.947E-3	-4.309E-5
C ₂ H ₆	4.854	205.7	5.197E-6	1.848E-2	-3.058E-4
C ₂ H ₂	8.088	110.2	1.126E-2	1.248E+0	-1.141E-1
C ₂ H ₄	4.770	185.3	1.060E-5	3.230E-2	-5.771E-4

**Figure 1: Comparison of Equation 1 with experimental data using both the optimized parameters in Table 1 and those in the original CHEMKIN database for nitrogen (left) and acetylene (right).**

for other researchers to implement in their own models. An example of our multivariate normal distribution fitting results is shown in Figure 2 for CH₄. The means, variances, and covariances of these multivariate normal fits are also available in our repository, and they will be regularly updated to reflect the latest additions of experimental data. Notably, the model in Equation 1 fails to satisfactorily reproduce experimental virial coefficient data for highly polar molecules, such as H₂O. This is not surprising; we did not account for permanent dipole moments in our model. These molecules have historically presented problems for transport parameter fitting even when more appropriate intermolecular interaction models (i.e., Stockmayer potential) are used [19].

3.2 Effects on flame speed and self-diffusion coefficients

The uncertainty results for three different atmospheric pressure CH₄-air flames are shown in Table 2. Although Ar was included in the list of species whose parameters were modified, it had no effect in these simulations because there was no Ar in the air and so is not listed in Table 2. In all cases, the inclusion of the Soret effect reduced flame speeds slightly. Though not shown here, it is noteworthy that the predicted flame speeds using our optimized transport parameters with the “relatively untuned” mechanism [26] are lower than those predicted using the transport parameters

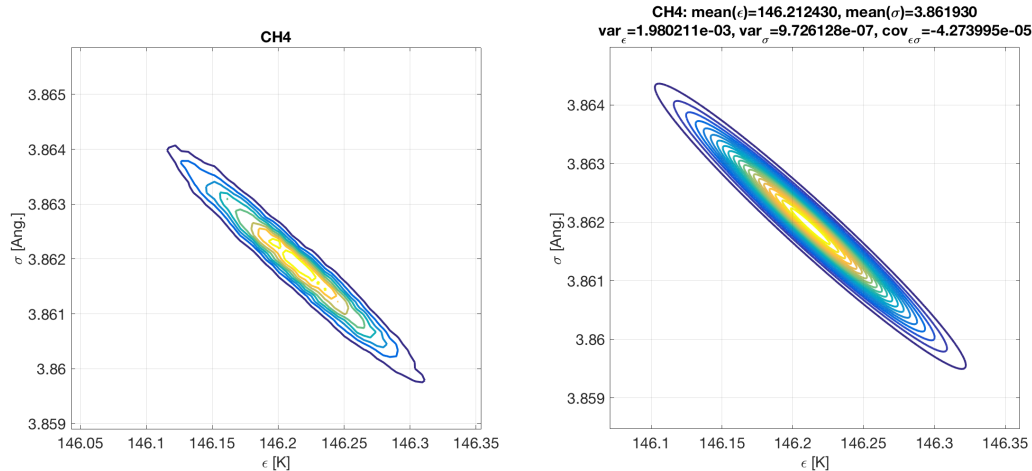


Figure 2: Example of joint posterior PDF generated from MCMC sampling (left) and a multivariate normal distribution fit (right) applied to the joint posterior PDF for CH₄, the parameters of which are listed in Table 1.

Table 2: Influence of the parameters of each species on 1 atm s_u^0 for different ϕ in [cm/s].

ϕ	s_u^0	$\Delta s_{u,tot}^0$	Δ_{CH_4}	Δ_{O_2}	Δ_{N_2}	Δ_{H_2}	Δ_{CO}	Δ_{CO_2}	$\Delta_{C_2H_6}$	$\Delta_{C_2H_2}$	$\Delta_{C_2H_4}$
0.60	8.6242	0.017	0.001	0.005	0.008	0.006	0.012	0.001	0.000	0.001	0.000
1.00	33.996	0.030	0.001	0.021	0.020	0.006	0.002	0.000	0.001	0.001	0.001
1.40	18.027	0.058	0.004	0.053	0.010	0.021	0.001	0.001	0.001	0.005	0.001

in the original CHEMKIN database [25] and much lower than those predicted using the GRI-MECH 3.0 [30] mechanism, especially for lean flames. The reasons for this are presently unclear, but highlight that chemistry and transport are intrinsically coupled in flame speed calculations. Example histograms of laminar flame speeds for lean, stoichiometric, and rich atmospheric flames resulting from the random transport parameter samples are shown in Figure 3 and are grouped by color according to the species whose parameters were varied. Consistent with previous observations [16], we found that the larger relative uncertainties in laminar flame speed occur more frequently for rich values of ϕ , and that, for all ϕ , the largest source of uncertainty is due to the uncertainty in the transport parameters of N₂ and/or O₂. In lean conditions, the uncertainty in the transport parameters of CO and H₂ play a more significant role in the overall flame speed uncertainty than at stoichiometric conditions, which was also known previously. The additions of the species C₂H₄, C₂H₆, and particularly C₂H₂ to our analysis increases the uncertainty over previous estimates at rich conditions, since these species predominantly show up in rich flames. Additionally, the inclusion of the Soret effect in the flame models in this paper increases the contribution to the overall uncertainty from H₂ for stoichiometric-to-rich ϕ over previous estimates.

Example histograms of the self-diffusion coefficients D_{jj} of H₂ and O₂ are shown in Figure 4. The effect of modifying transport parameters on diffusivities is larger in an absolute sense for light species like H₂, and smaller for heavier species like O₂. The histograms in Figure 4 appear to be normal distributions, but we cannot be certain with only thirty samples.

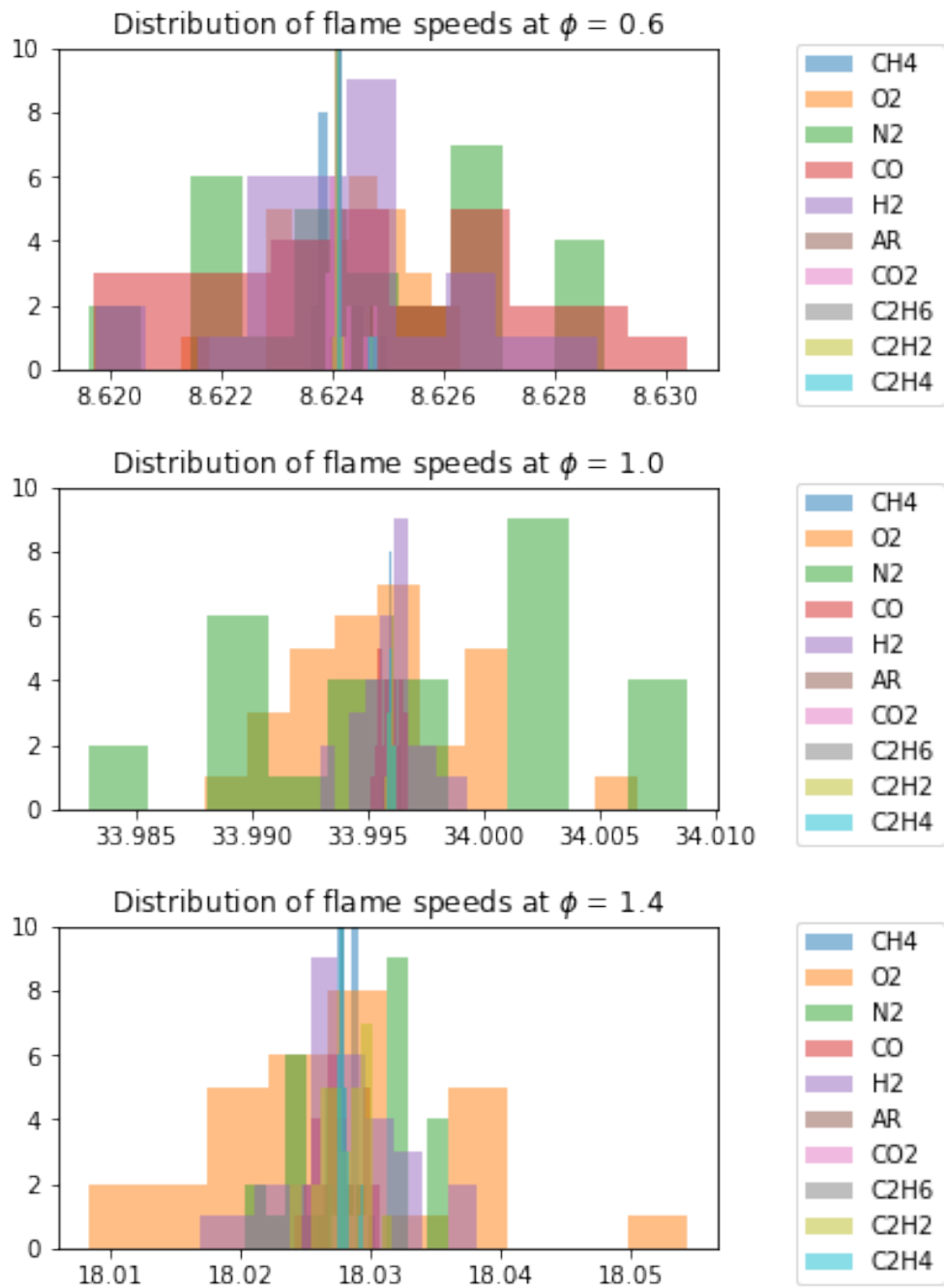


Figure 3: Visual representation of the effect of modifying transport parameters on flame speeds, grouped by species. The x-axis is flame speed in [cm/s].

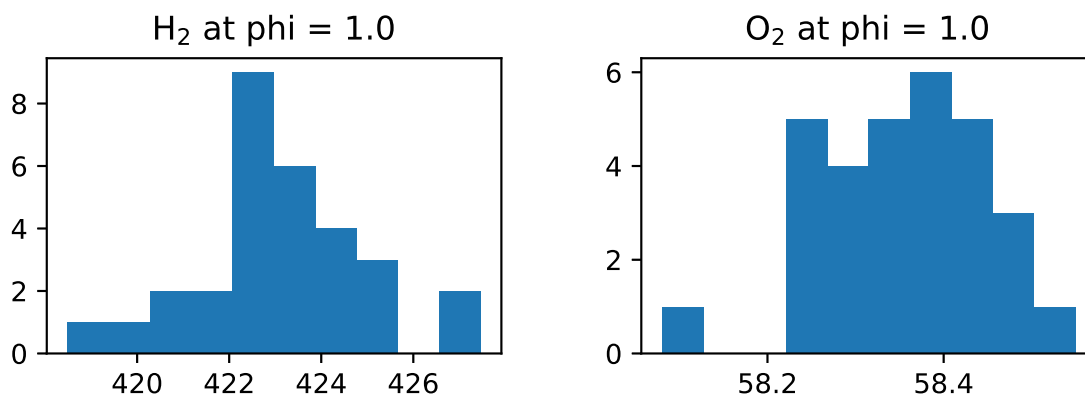


Figure 4: Visual representation of the effect of modifying transport parameters on species diffusivities for H₂ (left) and O₂ (right) at a flame temperature of 2216 K. The x-axis is diffusivity [cm²/s]

4 Conclusions

We are certainly not the first to notice that the properties listed in the original CHEMKIN database do not satisfactorily reproduce experimental results [28, 15] and do not make any claims of the sort. However, this work adds to the existing evidence that transport is not a solved problem in flame models. We noticed that flame speeds were overall lower after modifying the transport parameters in the mechanism, and we encourage the community to consider *both* the transport and the chemistry uncertainties in tandem when refining mechanisms for 1-D flames. Otherwise, chemical rate parameters might incidentally be adjusted such that fortuitous error cancellations mask underlying inaccuracies in the transport data. We note that we are not the first to express this word of caution [9]. Transport parameters derived from other physical measurements by others (e.g. from viscosity measurements by Mouritis & Rummens [19]) have slightly different values. For non-polar molecules, our MCMC-optimized $\sigma_{j,opt}$ are in decent agreement, but our $\epsilon_{j,opt}$ are slightly larger. This could be a consequence of experimental virial coefficient data being heavily weighted towards low temperatures, where stronger intermolecular interactions are more apparent [18]. For slightly polar molecules, our MCMC-optimized $\sigma_{j,opt}$ are in not-as-good agreement (very poor agreement for extremely polar molecules), and our $\epsilon_{j,opt}$ are in worse agreement. Luckily, first-order macroscopic properties are not that sensitive to ϵ_j [9]. Future studies will incorporate experimental viscosity data and models into our estimates for $\sigma_{j,opt}$ and $\epsilon_{j,opt}$.

The larger flame speed uncertainty for rich flames with the inclusion of more species that are often present in rich flames lends more support to the notion that rich combustion chemistry is not well characterized. Indeed, many mechanisms (particularly for larger fuels) deviate from experimental flame speed data [31], speciation data [32], or blow-off data [33] for very rich conditions. Inadequate transport parameter data/models for species that predominantly exist in these regimes may provide an explanation, and this will be the subject of future investigation.

Acknowledgments

DIP wishes to thank Rebecca L. Freund, Lianne Ippel, and Dr. Joris Mulder for helpful discussions regarding statistics.

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