Verification of nonequilibrium thermochemistry models for hypersonic CFD by first-principles simulation

E. Torres*, T. Gross*, E. Geistfeld* and T.E. Schwartzentruber*
Corresponding author: etorres@umn.edu

* Department of Aerospace Engineering and Mechanics, University of Minnesota
107 Akerman Hall, 110 Union St. SE Minneapolis, MN 55455-0153 USA

Abstract: In this paper, we present verification studies for the recently proposed Modified Morrone-Treanor [1] (MMT) thermochemical nonequilibrium model for computational fluid dynamics (CFD). We verify our CFD results using first-principles Direct Molecular Simulations (DMS) that rely only on potential energy surfaces (PESs) to determine all collision outcomes. Therefore, DMS is capable of naturally predicting vibrationally coupled excitation and dissociation of the gas under thermochemical nonequilibrium without any tuning parameters. The MMT model was developed using first-principles data for nitrogen and oxygen dissociation, but used existing model parameters for Zel'dovich reactions. The present research performs first-principles simulations that now include all important interactions for dissociated air, including Zel'dovich reactions. The results are used to verify the accuracy of the MMT CFD model for a range of post-shock conditions, and suggest further modifications to improve the model. This research demonstrates how complex nonequilibrium chemistry induced by hypersonic flight can be incorporated into accurate and efficient models for large-scale CFD simulations.

Keywords: Thermochemical nonequilibrium, Hypersonic flow, Computational Fluid Dynamics, Modified Marrone-Treanor model, Direct Molecular Simulation.

1 Preliminary results: Coupled vibration-dissociation of nitrogen and oxygen in space-homogeneous heat baths

The MMT model was originally implemented by Chaudhry et al. [1] into US3D [2], the state-of-the-art CFD code for hypersonic flow simulations developed at the University of Minnesota. The MMT kinetic rate parameters for N_2 and O_2 dissociation were generated from quasi-classical trajectory (QCT) calculations [3, 4] on the Minnesota *ab initio* potentials. The model was later employed in vehicle-scale simulations of hypersonic flows [5].

In the present verification study, we return to focus on simpler space-homogeneous heat baths (0D reactors) to verify the nonequilibrium chemistry in isolation. As a first test, we simulate the coupled vibration-dissociation of pure nitrogen and oxygen separately at several temperatures. Initial conditions for the nitrogen case were: $p_0 = 1.36\,\text{atm}$, $T_{\text{rot}} = T_{\text{vib}} = 300\,\text{K}$, whereas for the oxygen case the initial pressure was reduced to $p_0 = 0.81\,\text{atm}$. With the MMT model we employ

the rate coefficients for N_2–N_2, N_2–N, O_2–O_2 and O_2–O dissociation reported by Chaudhry et al. [1]. These rate coefficients were further adjusted to better simulating the post-shock environment by including so-called non-Boltzmann depletion factors. These factors, originally calibrated by means of DMS calculations, cause the effective dissociation rate coefficients to be between 2-4 smaller than the equivalent thermal ones, due to the depletion of high–lying vibrational states of N_2 and O_2 behind the shock front. We then repeated the same set of calculations employing the standard rate coefficients and T-T_v dissociation model of Park [6] for reference.

(a) nitrogen at $T = 10\,000\,\mathrm{K}$. (b) oxygen at $T = 5\,000\,\mathrm{K}$.
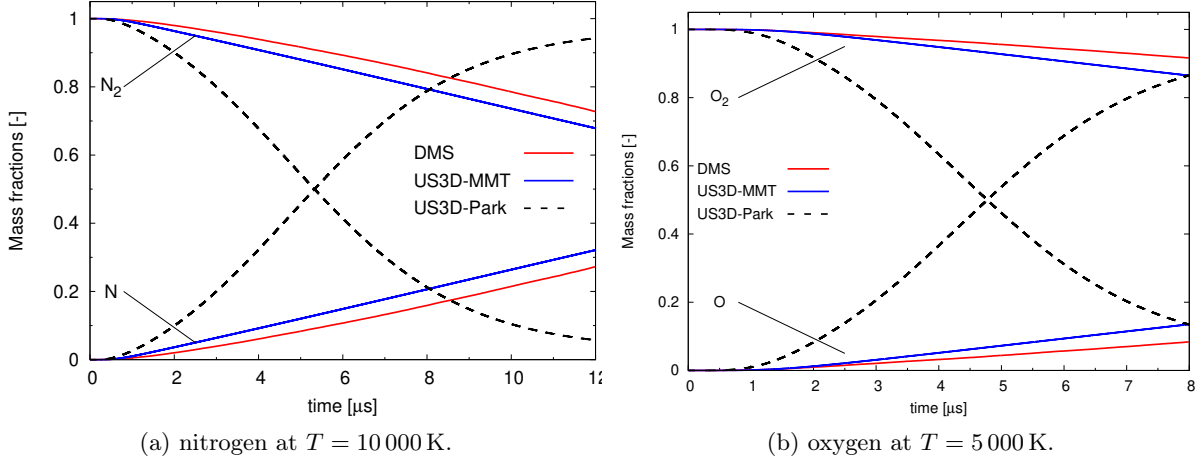
Figure 1: Coupled vibration-dissociation of N_2 and O_2 in isothermal heat baths: species mass fractions. Comparison of MMT (solid blue) and Park (dashed black) models with DMS (solid red).

As can be seen in Figs. 1a and 1b, there are significant differences in the reaction rates predicted with the two CFD models. For both the nitrogen and oxygen cases, the MMT model predicts dissociation rates several factors slower than the standard Park model. As would be expected, the behavior of the MMT model is much closer to the DMS predictions, given that the MMT kinetic rate parameters were originally calibrated with the help of first-principles QCT and DMS calculations.

2 Ongoing Work

We are currently in the process of re-calibrating the rate parameters for the Zel'dovich exchange reactions, $O_2 + N \rightleftharpoons NO + O$ and $N_2 + O \rightleftharpoons NO + N$ and integrating them into the MMT model. In addition to updating the reaction rates, our recent work [7] also revealed that the standard characteristic times for vibrational relaxation employed in current CFD codes often differ from the DMS predictions. The discrepancies become more significant at higher temperatures, where typically the standard Millikan and White correlation for τ_v [8] is no longer applicable and Park's high-temperature correction [6] is usually added. Updating the characteristic vibrational relaxation times should further improve the agreement of the MMT model predictions with our DMS benchmark. The goal of this paper is to suggest final adjustments to the MMT model, so that it is fully consistent with first-principles data. On-going research also aims to validate the model with recent experimental data [9, 10].

References

[1] R.S. Chaudhry, I.D. Boyd, E. Torres, T.E. Schwartzentruber, and G.V. Candler. Implementation of a Chemical Kinetics Model for Hypersonic Flows in Air for High-Performance CFD. In *AIAA Scitech 2020 Forum*, 2020. AIAA 2020-2191.

[2] G.V. Candler, H.B. Johnson, I. Nompelis, P.K. Subbareddy, T.W. Drayna, and V. Gidzak. Development of the US3D Code for Advanced Compressible and Reacting Flow Simulations. In *53rd AIAA Aerospace Sciences Meeting, Kissimmee, Florida*, 2015. AIAA 2015-1893.

[3] J.D. Bender, P. Valentini, I. Nompelis, Y. Paukku, Z. Varga, D.G. Truhlar, T.E. Schwartzentruber, and G.V. Candler. An improved potential energy surface and multi-temperature quasiclassical trajectory calculations of $N_2 + N_2$ dissociation reactions. *The Journal of Chemical Physics*, 143:054304, 2015.

[4] R.S. Chaudhry, J.D. Bender, T.E. Schwartzentruber, and G.V. Candler. Quasiclassical Trajectory Analysis of Nitrogen for High-Temperature Chemical Kinetics. *Journal of Thermophysics and Heat Transfer*, 32(4):833–845, 2018.

[5] R.S. Chaudhry, I.D. Boyd, and G.V. Candler. Vehicle-Scale Simulations of Hypersonic Flows using the MMT Chemical Kinetics Model. In *AIAA Aviation 2020 Forum*, 2020. AIAA 2020-3272.

[6] C Park. Review of Chemical-Kinetic Problems of Future NASA Missions, I: Earth Entries. *Journal of Thermophysics and Heat Transfer*, 7(3):385–398, 1993.

[7] E. Torres, E.C. Geistfeld, and T.E. Schwartzentruber. Direct molecular simulation of rovibrational relaxation and chemical reactions in air mixtures. In *AIAA SCITECH 2022 Forum*, 2022.

[8] R.C. Millikan and D.R. White. Systematics of Vibrational Relaxation. *Journal of Chemical Physics*, 39(12):3209–3214, 1963.

[9] J.W. Streicher, A. Krish, R.K. Hanson, K.M. Hanquist, R.S. Chaudhry, and I.D. Boyd. Shock-tube measurements of coupled vibration–dissociation time-histories and rate parameters in oxygen and argon mixtures from 5000 k to 10 000 k. *Physics of Fluids*, 32(7):076103, 2020.

[10] J.W. Streicher, A. Krish, and R.K. Hanson. Vibrational relaxation time measurements in shock-heated oxygen and air from 2000 k to 9000 k using ultraviolet laser absorption. *Physics of Fluids*, 32(8):086101, 2020.