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

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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: $p_0 = 1.36$ atm, $T_{\text{rot}} = T_{\text{vib}} = 300$ K, whereas for the oxygen case the initial pressure was reduced to $p_0 = 0.81$ atm. With the MMT model we employ...
the rate coefficients for \( \text{N}_2 - \text{N}_2 \), \( \text{N}_2 - \text{N} \), \( \text{O}_2 - \text{O}_2 \) and \( \text{O}_2 - \text{O} \) 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 \( \text{N}_2 \) and \( \text{O}_2 \) 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.

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, \( \text{O}_2 + \text{N} \rightleftharpoons \text{NO} + \text{O} \) and \( \text{N}_2 + \text{O} \rightleftharpoons \text{NO} + \text{N} \) 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 \( \tau_v \) [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


