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# Validation of Models via Comparison with Data for Non-equilibrium Near- Continuum Hypersonic Flows

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Ingrid J. Wysong

Sergey F. Gimelshein (Jacobs)

Air Force Research Laboratory (AFMC)  
Combustion Devices Branch  
AFRL/RQRC  
10 E. Saturn Blvd.  
Edwards AFB, CA 93524

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In-House Final Report

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## **Summary**

This final report summarizes the effort from Work Unit Q1MK. The Work Unit consisted of two 3-year Air Force Office of Scientific Research (AFOSR) Lab tasks. The first, titled "Validation of models via comparison with data for non-equilibrium near-continuum hypersonic flows" covered FY16 – FY18. The second continued the research of the first task, titled "Determination of Key Physics for Non-equilibrium Modeling of Hypersonic Air," and covered FY19 – FY21.

The report consists of the Final Reports submitted to AFOSR for each of the two Lab Tasks. All of the technical details of the work are contained in the 20 peer-reviewed journal articles that are listed.

# Final Report FY16-18

**LRIR Number:** 16RQCOR262

**Lab Task Title:** Validation of models via comparison with data for non-equilibrium near-continuum hypersonic flows

**Principle Investigator:** Ingrid Wysong

**Co-Investigator:** Sergey Gimelshein

## Summary of Accomplishments

The team has studied the impact of increasing the fidelity of high temperature molecular collision models on key surface, flow, and signature properties for AF-relevant hypersonic conditions. In this work, we have leveraged the high fidelity real gas effect kinetic models developed over the first two years, and applicable to particle simulations and specifically the direct simulation Monte Carlo (DSMC) method. The models include vibrationally coupled dissociation and recombination, 3D forced harmonic oscillator (FHO) for vibration-translation (V-T) energy transfer, and the near-resonant vibration-vibration (V-V) transitions. Several research directions have been pursued to achieve the goals.

(i) The impact of the high temperature model on the hypersonic air flow properties has been assessed. To this end, two DSMC models are examined and compared to quasi-classical trajectory (QCT) results and experimental measurements: the conventional model based on the Larsen-Borgnakke approach to energy transfer and the total collision energy of chemical reactions of dissociation and exchange, and a high-fidelity model. The latter one incorporates the FHO-FR model of V-T energy transfer, a general V-V energy transfer model, the vibrationally coupled Bias dissociation model, and a consistent recombination process. The flow conditions were used to match the well known experimental facilities T5 (I. Leyva and H. Hornung), LENS XX (M. Holden with collaborators), and HEG (S. Karl with collaborators), with free stream velocities ranging from 3 to over 6 km/s, and pressures on the order of several torr. Several conclusions were drawn from the obtained numerical results. First, a simple Bias model provides sufficient accuracy to quantitatively capture the main features of dissociation of air species. Second, the impact of refinement of internal energy transfer and chemical reaction model is relatively minor for both flow fields and surface properties. V-V and V-T models were found to provide little impact on gas and especially surface properties. Available experimental data may not offer the means necessary to distinguish between the models, and reducing experimental error bars down to 5% or below may be necessary in order to accomplish that task. Third, the impact of gas-phase recombination in the vicinity of the wall was shown to be dominant for a flow over a cylinder, and more study of that process, often omitted in DSMC, may be necessary.

(II) As mentioned above, the near-wall gas-phase recombination was found to be very important for accurate production of surface heat loads. Therefore, the combined impact of both the gas-phase and the surface catalytic recombination reactions on the heat flux was examined in detail for a hypersonic air flow over a cylinder for a wide range of gas densities and flow velocities. The numerical modeling was again performed using the DSMC method, since it provides physically realistic temperature jump conditions at the wall, and allows one to resolve the thermally and chemically non-equilibrium flow near the wall. Comparison of the simulation results for HEG I conditions showed good agreement with measured heat fluxes when both gas and surface reactions are included in simulations. For the baseline condition of  $Kn=0.001$ ,  $U=6$  km/s, the gas-phase nitrogen recombination reactions were found to have a determining impact on the heat flux. The impact of a fully catalytic wall is also significant but smaller. The influence of the dissociation model and the equilibrium constant on the heat flux was found to be minor. The free stream Knudsen number and velocity were varied between 0.0005 and 0.003, and 4 and 8 km/s, respectively. Such a variation was shown to significantly affect the relative contribution of the gas and surface recombination reactions. For Knudsen numbers of 0.001 and lower, gas recombination dominates, while the surface reactions are more important for more rarefied flows. The contribution of gas recombination increases with flow velocity, being negligible at 4 km/s and becoming the most important inelastic collision process at velocities of 6 km/s and higher.

Another key parameter that impacts gas recombination was shown to be the surface temperature. At temperatures below 1000 K, such a recombination is very important, and results in significant, up to a factor of two, increase in the heat flux. Its contribution considerably decreases at higher surface temperatures, and becomes negligible at

a temperature higher than 2000 K. The maximum heat flux at the stagnation point is approximately three times lower for a non-catalytic 2000 K wall than for a catalytic 300 K wall.

(III) In addition to a comprehensive analysis of high temperature air model on flow and surface parameters, the team has used the DSMC method to analyze the impact of different high temperature processes and models on radiance intensities and spectra in reacting air. In addition to conventional and high fidelity recombination-dissociation and vibrational energy transfer models above, we have also used a conventional and an advanced models for the key  $N_2+O$  exchange reaction. The numerical simulations were focused on a reflected shock wave, with flow conditions that reproduce shock-tube experiments of Treanor in nitrogen-oxygen mixtures, and Cruden and Brandis of NASA Ames, in air.

Comparison with IR intensities measured by Treanor et al in a shock tube was conducted for free stream velocities between 2.97 and 3.87 km/s. For that flow regime, the impact of all collisional models was shown to be small, and both conventional and high fidelity approaches provided good agreement with the data and with the solution of the master kinetic equations of Adamovich with co-workers. It was therefore concluded that the simplified conventional models are adequate for such a low-temperature regime. The computations for a significantly higher flow velocity, and thus non-equilibrium, case of 6.81 km/s, and comparison with the ultraviolet (UV) spectra obtained by Cruden and Brandis in an after-shock region, indicated that the conventional model performs poorly, whereas the high fidelity model developed by the team provides good agreement with the experimental data. The analysis has shown that there are several aspects that warrant further investigation. The energy disposal after  $N_2+ON \rightleftharpoons O+N$  reaction, and in particular the population of higher vibrational levels after that reaction, is important as it impacts the vibrationally favored dissociation of nitric oxide (NO). The equilibrium constant for the above reaction may need further refinement as it impacts both concentration and vibrational temperature of NO. Taking into account vibrational favoring in dissociation reactions, especially for molecular nitrogen, strongly impacts gas temperatures, and thus NO concentrations, behind the shock. While excellent agreement between the high fidelity approach and the measured spectra was obtained, additional research may be necessary to complete model validation, ideally including experimental data on transient NO intensity for different velocities and gas compositions in UV and IR spectral regions.

(IV) Recent experimental data of Shatalov with co-workers on vibrational temperature in strong  $O_2$  shock waves, based on UV absorption measurements, recently attracted significant attention in the computational fluid dynamics (CFD) community. Despite an apparent simplicity of the physical setup, the agreement between modeling and data, and the general success in model validation, has been mixed so far. The difficulty of matching the data has raised questions to the accuracy of some numerical models as well as numerical and experimental error bars. The latter ones to a large degree are related to the accuracy of conversion of UV absorption to vibrational temperatures. The experimentalists have used two simplifying assumptions when deriving vibrational temperatures from their absorption spectra: (i) the equality of translational, rotational, and electronic temperatures, and (ii) Boltzmann populations of rotational and vibrational energy modes and electronic levels of molecular oxygen. Since the validity of these assumptions in the strongly non-equilibrium conditions of the experiments is not at all obvious, our team has extensively tested them.

Our numerical modeling provided the vibrational and rotational populations, as well as mode temperatures, as an input for the subsequent evaluation of absorption spectra in the Schumann-Runge range of wavelengths, conducted by N. Bykova. The team's numerical results have shown that the impact of non-Boltzmann populations on the computed spectra, and thus on the vibrational temperature obtained from that spectra, is considerable only upstream from the location of the maximum vibrational temperature. The error in absorption computed using the Boltzmann assumption is up to an order of magnitude in that upstream region. The largest impact, up to 90%, comes from the vibrational non-equilibrium. The computed time-dependent absorption using realistic rovibrational populations is compared to the available measurement. The results are found to be in good agreement, especially for the maximum absorption.

(V) With the essential support and guidance from AFOSR, significant progress has been made over the last few years toward improving accuracy of numerical analysis of high temperature non-equilibrium gas flows. Recent availability of QCT-based state-specific rates and detailed cross sections, complemented by many proposed relaxation and reaction models, as well as the presentation of new experimental data on non-equilibrium high temperature flows, provides the solid basis and motivation in the non-equilibrium CFD community for adopting a common set of

benchmark cases. Similar to GEC RF Reference Cell in the plasma physics community, such benchmarks would elucidate both the validity of various approaches and the underlying reasons for differences in results.

Our team has lead the effort in this direction, and introduced Hypersonic Non-Equilibrium Comparison Cases (HyNECC) for non-equilibrium CFD methods.

The scope of HyNECC goes well beyond simple code-to-code comparison, and its main goals are:

- Comparison of reaction and relaxation rates produced by different models and implementations
- Projecting the differences and similarities in models and rates onto realistic non-equilibrium hypersonic flow conditions
- Comparison with available experimental data in order to understand how well or poorly state-of-the-art solvers predict different flows
- Finding properties and conditions most indicative and most sensitive to models, parameters, and implementations
- Providing specific feedback to the experimental community on conditions, properties, and flows of interest.
- Establishing clear, straightforward set of benchmarks for future code and model development

HyNECC includes test cases of various complexity, from 0D to 1D to 2D, with the current primary focus on non-ionized high temperature air flows.

## **Publications:**

Gimelshein, S. F., & Wysong, I. J. (2019). Nonequilibrium air flow predictions with a high-fidelity direct simulation Monte Carlo approach. *Physical Review Fluids*, 4 (3), 033405.

Gimelshein, S. F., & Wysong, I. J. (2019). Validation of high-temperature air reaction and relaxation models using emission data. *Journal of Thermophysics and Heat Transfer*, 33 (3), 606-616.

Gimelshein, S. F., & Wysong, I. J. (2019). Gas-phase recombination effect on surface heating in nonequilibrium hypersonic flows. *Journal of Thermophysics and Heat Transfer*, 33 (3), 638-646. <https://doi.org/10.2514/1.T5556>

Wysong, I. J., Gimelshein, S. F., Bykova, N. E., Shatalov, O. P., & Zabelinski, I. E. (2019, August). Impact of flow non-equilibrium in oxygen shock absorption analysis. In *AIP Conference Proceedings* (Vol. 2132, No. 1, p. 180008). AIP Publishing LLC.

Wysong, I. J., & Gimelshein, S. F. (2019, August). Hypersonic non-equilibrium comparison cases. In *AIP Conference Proceedings* (Vol. 2132, No. 1, p. 100008). AIP Publishing LLC.

Gimelshein, S. F., & Wysong, I. J. (2018). Modeling of Vibration-Vibration Energy Transfer in the DSMC Method. *Journal of Thermophysics and Heat Transfer*, 1-8.

Gimelshein, S. F., Wysong, I. J., & Adamovich, I. V. (2017). Direct Simulation Monte Carlo Application of the Three-Dimensional Forced Harmonic Oscillator Model. *Journal of Thermophysics and Heat Transfer*, 1-10.

Gimelshein, S., & Wysong, I. (2017). DSMC modeling of flows with recombination reactions. *Physics of Fluids*, 29 (6), 067106.

Gimelshein, S. F., & Wysong, I. (2017). Modeling hypersonic reacting flows using DSMC with the Bias reaction model. In *47th AIAA Thermophysics Conference*, AIAA Paper 2017-4025.

Wysong, I. J., & Gimelshein, S. F. (2016, November). Comparison of DSMC reaction models with QCT reaction rates for nitrogen. In *AIP Conference Proceedings* (Vol. 1786, No. 1, p. 050021).

Tumuklu, O., Levin, D. A., Gimelshein, S. F., & Austin, J. M. (2016, November). Factors influencing flow steadiness in laminar boundary layer shock interactions. In *AIP Conference Proceedings* (Vol. 1786, No. 1, p. 050005).

Tumuklu, O., Levin, D. A., Gimelshein, S. F., & Austin, J. M. (2016, November). Modeling of near-continuum laminar boundary layer shocks using DSMC. In *AIP Conference Proceedings* (Vol. 1786, No. 1, p. 050004).

# Summary Report FY2019-2021

**Lab Task:** 19RQCOR001

**Lab Task Title:** Determination of Key Physics for Nonequilibrium Modeling of Hypersonic Air

**Principal Investigator:** Ingrid Wysong, AFRL/RQRC    **Co-Investigator:** Sergey Gimelshein

## Brief Overview of Accomplishments and Results

**HyNECC:** We have led a multi-team research effort toward the development of Hypersonic Non-Equilibrium Comparison Cases (HyNECC) for non-equilibrium CFD methods. The effort included a multi-parametric study of high temperature oxygen, nitrogen, and air flows by different CFD approaches, from conventional continuum to state-to-state to fully kinetic, with a number of non-equilibrium reaction and excitation models. *Collaborators: D. Andrienko (TAMU), K. Hanquist (U Arizona), E. Kustova (SPSU, Russia), M. Fossati (U Strathclyde, UK)*

**Takeaway:** Comparison of state-specific and two-temperature approaches show there are very significant differences in the time-dependent nonequilibrium reaction rates. A major impact of the vibration-dissociation coupling on the temporal relaxation of gas properties is shown. Park 2T model fails at highly non-equilibrium conditions. Order of magnitude differences in the nitric oxide dissociation and recombination rates have a large impact on the peak NO mole fraction immediately behind the shock and surface distributed heat flux, respectively. High fidelity kinetic and continuum approaches are found to have different reaction channels having the largest effect on species mole fractions and gas temperature:  $N_2+O$  exchange and  $O_2+O$  dissociation in the former, and  $NO+O$  and  $O_2+N_2$  dissociation, in the latter. There is little impact of uncertainties in  $N_2$  dissociation.

**Reflected shock:** We have developed a CFD/DSMC approach which accurately captures the reflection of strong shock waves in a shock tube, and thus provides a path for the validation of high temperature non-equilibrium CFD models. The approach was applied for the analysis of modeling versus experiment validation issues and the testing of most widely used DSMC models in argon-oxygen and air mixtures. *Collaborators: R. Hanson, J. Streicher, A. Krish (Stanford U)*

**Takeaway:** Reflected shock configuration is shown to be a nearly ideal platform for model validation. Any comprehensive model validation using reflected shock data needs to account for gas interaction with the end wall and non-equilibrium of vibrational distribution for levels probed in the experiments. Proper account of electronic excitation is highly desirable. The Bias reaction model of DSMC is superior to the conventional Total Collision Energy (TCE) and Quantum Kinetic (QK) models. Modeling versus experiment differences in air warrant additional studies focused on Zeldovich reaction rates and oxygen-nitrogen vibrational excitation and non-equilibrium dissociation rate.

**Nozzle expansion:** This is the first application of a fully kinetic method to model a high-enthalpy converging-diverging nozzle flow. A 1D DSMC approach is developed, validated, and applied to examine the impact of flow non-equilibrium along the nozzle axis for several hypersonic flow facilities and carrier gases. *Collaborators: R. Hanson and C. Strand (Stanford U), J. Austin and H. Hornung (Caltech)*

**Takeaway:** The proposed kinetic approach is validated, and shown to be accurate and efficient. As expected, there is little impact of non-equilibrium in Caltech's T5 due to the high density conditions, but there is significant sensitivity of NO density to all exchange reaction and NO recombination rates. The use of the most recent theoretical and experimental rates results in a factor of two lower NO density at the nozzle exit as compared to the conventional Park rates. Multi-parametric sensitivity study of T5 conditions has not provided an explanation for a large drop in free-stream temperature and NO density over time, under constant flow velocity, observed recently in T5.

**Ionized flow:** Our DSMC capability has been extended to include ionization reactions, and to conduct a multi-parametric study of the impact of 7 and 11 species air models as compared to the standard 5 species model in a range of flight altitudes and speeds, thus providing the applicability areas for these models to predict aerothermodynamic properties of a RAM-C sphere-cone.

**Takeaway.** For bulks gas properties and surface fluxes, the 5 species model ignoring ionization is reliable up to 7 km/s. Ionization noticeably changed flow properties inside the shock at velocities of 9km/s and higher, and in the boundary layer, 8km/s and higher. The 7 species model is generally applicable for predicting peak electron density up to 8km/s. For higher velocities, it differs significantly from the 11 species model, especially inside the boundary layer, and underpredicts the heat flux reduction due to ionization by a factor of two.

**Oxygen shock:** This work was a completion of our multi-year effort aimed first at the validation of DSMC non-equilibrium reaction models, and then at the elucidation of differences observed between O<sub>2</sub> vibrational temperatures computed by several CFD teams and those obtained from shock-tube absorbance measurements. *Collaborators: N. Bykova and O. Shatalov (MSU, Russia).*

**Takeaway.** It is better to validate models by comparing directly to measured absorbance profiles, and not deduced  $T_{\text{vib}}$ . Low-M data from MSU are inaccurate after the peak absorbance. Bias DSMC model works well in capturing the measurements.

**Gas-phase recombination:** Recombination model developed in our previous lab task was applied to study nitrogen-oxygen flow over a cylinder, and the effect of gas-phase recombination reactions on distributed surface properties and gas macroparameters. The results are obtained with the direct simulation Monte Carlo method, and validated through the comparison with available surface heat flux and pressure data.

**Takeaway.** The recombination of nitrogen atoms in the vicinity of the wall makes a significant, over 40%, contribution to the heat flux near the stagnation point. The increase of the free stream density from 0.5 to 3g/m<sup>3</sup> and velocity from 4 to 8km/s makes that contribution even bigger. For higher flow velocities, recombination also increases the skin friction force. Analysis of the sensitivity of results to the surface temperature  $T_w$  shows that while the recombination rate decreases for higher  $T_w$ , it is still noticeable even for  $T_w=2000\text{K}$ , where it contributes up to 20% to the heat flux.

## Detailed Research Results

### 1. HyNECC

#### Analysis of Binary Gas Mixtures

Multiple two-temperature CFD, vibrational state-specific, and fully kinetic solvers have been applied to model thermal and chemical processes in high-temperature oxygen and nitrogen adiabatic heat baths. In the baseline analysis, the solvers used their standard vibrational excitation and reaction models and constants. Comparison of single-temperature and non-equilibrium rates show that the largest differences are observed for molecule-atom vibration-translation relaxation and N<sub>2</sub>-N<sub>2</sub> dissociation, especially at higher temperatures. High-accuracy shock-tube data, currently nonexistent, may be required to address these differences. For oxygen, state-of-the-art theoretical and experiment-based relaxation rates are relatively close, and differences associated in simulated flow fields using them may well fall below instrumental detection limits for the 5,000K-10,000K temperature range. Still, further refinements to the O<sub>2</sub>-O vibrational relaxation times and dissociation from the experimental and computational communities may prove to be useful. This is especially so if some light may be shed onto the vibrational favoring of dissociation reactions and the details of the relaxation of vibrational populations behind strong shocks, both shown to be important in this work.

Detailed comparison of oxygen relaxation modeled with vibrational state-specific and two-temperature approaches shows that there are very significant, and often qualitative, differences in the time-dependent non-equilibrium reaction rates, as well as their ratios to the corresponding single-temperature rates. For all three state specific solvers, which include master equation-based approaches and the fully kinetic direct simulation Monte Carlo method, there is a well-defined plateau observed at a time when the gas vibrational temperature approaches the translational temperature, and the thermal relaxation proceeds through a quasi-steady-state. Such a plateau is attributed to the depopulation of high vibrational energy levels due to dissociation, as such depopulation has little impact on temperature dominated by lower vibrational levels, but disproportionately high impact on the reaction rates.

There is no such plateau observed in the two-temperature solutions, although there is a peak, likely model-related, recorded before the gas comes to equilibrium. There are also qualitative differences observed in the transient profiles of the vibrational energy loss to dissociation. The two-step increase of that property in the state-specific

approaches is not captured in the continuum CFD, where the models show either a flat or a non-monotonous increase. All such differences may have significant implications for any hybrid approach that attempts to couple a continuum and a state-specific or a fully kinetic method.

The computations of oxygen and nitrogen baths show a major impact of the vibration-dissociation coupling on the temporal relaxation of gas temperatures, both translational and internal. Some differences in this coupling may need to be addressed in the future, such as the strongly non-linear behavior of the non-equilibrium reaction rate with vibrational temperature in the widely used Park's reaction model, versus the nearly linear shape for all state-specific approaches. Differences in molecule-molecule versus the molecule-atom vibrational coupling may also require some attention. The impact of the numerical approach on species mole fractions was found to be more significant in oxygen than in nitrogen.

Analysis of vibrational level populations in the strongly thermally non-equilibrium region show the profound impact that the choice of the numerical approach and model has on the population ratios, and thus vibrational temperatures inferred from such ratios. The difference in the absorption coefficients calculated by a temperature-based NEQAIR code using vibrational temperatures inferred from the populations of levels 4 and 6, computed by different state-specific and kinetic approaches, is found to exceed an order of magnitude. This may significantly complicate model validation when comparing to measured temperatures, and may also require a state-specific spectral code to be used when comparing computed and measured absorption spectra.

## **Analysis of Air Flows**

### *Reaction Rates*

Large uncertainties in vibrational relaxation and reaction rates for atomic and molecular air species, which are especially significant under conditions of strong thermochemical non-equilibrium, are associated with the lack of accurate and detailed experimental data on these processes. Ideally, each of these processes need to be evaluated individually in a wide range of flow conditions. In the absence of such data, CFD modelers usually choose rates and models that they believe best reflect the state of the art. Because of this, the five different solvers applied in this work use their standard rates and models as the baseline. Comparison of vibration-translation relaxation times assumed or applied in these solvers indicates that for a range of temperatures relevant to hypersonic simulations, there are large, in most cases well over an order of magnitude, uncertainties in collisions that include nitric oxide. There are also an order of magnitude differences for the important  $N_2+O$  interaction. Analysis of the reaction rate constants shows that there is good agreement between all solvers for Zeldovich exchange reactions. Similarly, there is little difference in the assumed equilibrium constants. The largest, up to two orders of magnitude, differences are observed between the NS and the three state-to-state approaches for the dissociation and recombination reactions of NO. The corresponding rate constants of both NS solvers, which are conventionally based on Park's recommendations, systematically overpredict the other three, which are based on recent theoretical predictions.

### *Moderate Temperature 0D and 1D Relaxation*

The moderate temperature adiabatic bath relaxation, where the initial translation-rotation temperature is on the order of 7,000K, is the test case where all solvers and models considered here are used. The computations have clearly shown that there is better agreement in gas temperatures, both translational and vibrational, than in species mole fractions. In the latter, the differences in relaxation time reach an order of magnitude, and the culprit to a large extent was oxygen dissociation on  $N_2$  molecules. For this collision type, more complete and accurate information on vibration-dissociation coupling may be required, applicable to both state specific and traditional continuum approaches.

Besides 0D heat bath, DSMC computations were also conducted of a 1D reflected shock wave where experimental data have recently been obtained on oxygen absorbance under conditions similar to those of the moderate temperature heat bath case. The computations indicate that a reconsideration of the relaxation properties of the currently used vibration-vibration model may be needed, originally developed based on experimental data obtained at much lower temperatures. The baseline DSMC model was found to capture well the initial rise in absorbance, and the absorbance maximum, but not the sharp decrease after the peak. Comparison of 1D and 0D results indicates that such a decrease may be difficult to capture for all state-to-state approaches considered here. The

NS approaches cannot be applied for this comparison as long as they use a two-temperature model; a separation of vibrational temperature by species would be necessary in this case (or in any case where O<sub>2</sub> or NO vibrational temperature or absorbance is measured inside a shock).

### *High Temperature 0D and 2D Relaxation*

The distinctions between solvers significantly when the adiabatic bath temperature was increased to 15,000K. Most notably, there is an over a factor of two difference between the maximum mole fractions of NO. It is much higher in DSMC and the QCT based solution of the vibrational kinetic equations than in NS, with the primary reason being two orders of magnitude higher NO dissociation rates assumed in NS. There are also noticeable differences in the time-dependent profile of atomic oxygen mole fraction, with the state-specific approaches indicating a change of slope related to gas reaching quasi-steady state, and dissociation slowing down due to the depopulation of high vibrational levels. The computations allowed the evaluation of separate contributions of different reaction channels to the time evolution of O<sub>2</sub> and NO mole fractions and gas temperature. These contributions were found to be qualitatively different, with the main players being N<sub>2</sub>+O exchange and O<sub>2</sub>+O dissociation in DSMC, O<sub>2</sub> dissociation on N<sub>2</sub> in a vibrational state specific approach, and NO+O dissociation, in addition to O<sub>2</sub>+N<sub>2</sub> dissociation, in NS.

DSMC simulation of a hypersonic flow over a cylinder shows that, for considered conditions, the non-equilibrium gas model, which includes vibration-dissociation coupling and a high-fidelity treatment of vibration-translation energy transfer, has visible impact on the gas properties inside and immediately behind the shock, as well as the shock stand-off distance, but has virtually no effect on the distributed aerothermodynamic properties. Reaction rate constants do impact gas properties and surface heat flux for both DSMC and NS. For the gas properties, the large uncertainties in the dissociation rates of NO have a dominant impact on the peak NO mole fraction. For the heat flux, NO recombination becomes a major player, in addition to nitrogen dissociation. Generally, there is good agreement between NS and DSMC heat fluxes, both for lower-fidelity models based on Park's reaction rate constants, and higher-fidelity QCT based models. Peak heat flux for a higher fidelity model in NS is approximately 10% lower than its lower fidelity counterpart, with the difference attributed to the dissociation rate constants. NS and DSMC models that include surface catalycity agree well with available experimental data on surface heat flux, although this agreement may not be regarded as a comprehensive model validation, for which detailed spectrally and spatially resolved experimental data would be necessary.

### *Code-to-Code Differences*

In the ideal case of fully defined and consistent physical and chemical models applied in different CFD solvers, with matching rates and compatible models, differences in the results would be negligible. This is often not the case, though, as the results are also influenced by various numerical parameters. An example of this effect were shown in this work, where the application of two NS solvers with identical physical models resulted in virtually identical results in adiabatic baths, but visibly different stand-off distances for a hypersonic flow over a cylinder.

### *Effect of Vibrational Relaxation and Reaction Model*

Multiple comparisons presented in this work illustrate how the uncertainties in relaxation and reaction rates are exacerbated by uncertainties related to non-equilibrium collision and reaction models. In NS solvers, changing nonpreferential to preferential model of vibrational energy lost to dissociation has visible, but still relatively small, impact on gas relaxation. However, replacing the conventional 2D-Park reaction model to MMT has large effect both on overall and species properties, where the MMT relaxation is several times slower than 2T-Park. Similar, in DSMC, the vibrationally favored Bias dissociation model results in much slower relaxation than the conventional TCE model, and this model effect is sometimes larger than the effect of the rates. While it is tempting to conclude that Bias model in DSMC and MMT model in NS better capture the properties of real reacting air than their simpler conventional counterpart, as they certainly offer improved physical realism, certain caution needs to be used before such a conclusion is drawn. The reason being the lack of detailed parametric validation of these models with accurate and time-resolved experimental data in a sufficiently wide range of temperatures.

### *Validation: What is Missing?*

With the impressive progress achieved over the last decade at shock tube facilities, where time-accurate emission and absorption diagnostics were applied behind incident shock waves (NASA EAST and Moscow State facilities) and, most recently, reflected shock waves (Stanford reflected shock facility) at highly non-equilibrium, hypersonic

conditions, the daunting task of non-equilibrium high-temperature air model validation may finally be within reach. For validation efforts to be successful, time-resolved diagnostics with error bars within 5% would be highly desirable, in the range of temperatures from 5,000K to 15,000K. In this work, several aspects that would be useful for such a validation are highlighted,

- Nitric oxide relaxation and dissociation properties
- Vibration-translation energy transfer in collisions of atoms with  $N_2$ , as well as  $N_2$  dissociation rate
- Peak nitric oxide mole fraction behind strong shock waves
- Vibrational favoring of  $N_2$ ,  $O_2$ , and  $NO$  dissociation
- Reaction paths most important in moderate and high temperature regimes

## 2. Reflected Shock Wave

The direct simulation Monte Carlo method is used to examine the flow behind a reflected shock wave. The simulated flow conditions reproduce the conditions of recent experiments conducted in Stanford shock-tube facility, where absorbance time histories in the Schumann-Runge UV band of  $O_2$  were recorded behind a reflected shock in oxygen-argon, pure oxygen, and air gas mixtures, with after-shock temperatures ranging from 3000K to 14000K. The present numerical approach captures the transient reflection of an incident shock on the end wall of the shock tube, with fill gas properties and incident shock velocities corresponding to those in the experiments, thus minimizing the impact of the numerical setup.

Two objectives are pursued in this work. First, physical and numerical factors that may impact the validation of the computational model are investigated, which include energy accommodation at the end wall, gas relaxation in the incident shock, the location of the observation point, the electronic excitation of atoms and molecules, and non-equilibrium populations of vibrational levels probed in the experiments. Second, the impact of non-equilibrium vibration-translation excitation and dissociation models on observable gas properties are studied. For the former, the Larsen-Borgnakke and 3D Forced Harmonic Oscillator models are applied. For the latter, three most widely used DSMC chemistry models are used, the Total Collision Energy model, the Quantum Kinetic model, and the Bias model.

The first step in the parameter analysis and model-to-data comparisons was matching equilibrium and non-equilibrium rates used in the computations with those recommended in the corresponding  $O_2$  absorbance experiments. In equilibrium gas, the rate matching focused on the vibrational relaxation times and single-temperature dissociation rate constants of  $O_2$  colliding with argon,  $O_2$ ,  $O$ , and  $N_2$ , as well as the vibration-vibration energy transfer between  $O_2$  and  $N_2$ . Such matching included both V-T models, and the TCE and Bias models. For the original QK model, there are no adjustment parameters which control the dissociation rate. Because the QK rates were found to significantly overpredict the data, in addition to the original QK model, computations were conducted for QK with reaction rates adjusted through the multiplication of reaction probabilities by a constant species-dependent factor to match the databased recommendations. Comparison of the V-T relaxation times indicates that the relaxation governed by the conventional Millikan-White-Park model could be too fast for  $N_2$ - $N_2$  collisions, where new data is needed for temperatures larger than 6000K.

At non-equilibrium, where the vibrational temperature is lower than the translation-rotational temperature, only the parameters of the Bias reaction model were adjusted, as it was the only model used here which explicitly incorporates the effect of vibration-dissociation favoring. Non-equilibrium oxygen-argon and pure oxygen baths were considered, with temperature conditions matching those of the absorbance experiments. The Bias model was found to reproduce well the databased non-equilibrium dissociation rate constants and the average vibrational energies of dissociating molecules for the range of temperatures considered here. Poor modeling versus experiment agreement was observed when these properties are computed with the TCE and QK models. Both models overpredict the non-equilibrium dissociation rates, and underpredict the average vibrational energy loss to dissociation.

Analysis of factors which may complicate model validation have shown that a non-specular energy accommodation at the end wall noticeably, up to 10%, decreases the velocity of the reflected shock, reducing the dissociation rate behind the shock and, to a lesser degree, the gas temperature. Experimental assessment of an effective accommodation coefficient is therefore highly desirable. Modeling of the shock reflection at the end wall have

shown that at higher incident shock velocities, the thermochemical relaxation behind the incident shock becomes significant, thus complicating data interpretation. The location of the observation point has little impact on flow observables, as long as the boundary layer has not reached that point. At 5mm from the wall, test times may be limited to 100 $\mu$ s. On the other hand, accurate characterization of gas-surface interaction, if available, may provide an opportunity for studying the boundary layer. The electronic excitation, expected primarily for oxygen molecules, was found to have visible effect on the flow, especially on species mole fractions. Accurate modeling of such an excitation, which goes beyond a Larsen-Borgnakke type approach with constant electronic excitation numbers, would be highly desirable for reliable calibration of high temperature collision models. The approach used to compute vibrational temperatures was found to have large effect on oxygen vibrational temperature time histories; the account for the actual populations of vibrational levels probed in the experiments is necessary for absorbance computations and model validation.

Modeling of gas relaxation behind a reflected shock have shown almost negligible effect of O<sub>2</sub>-N<sub>2</sub> vibration-vibration energy transfer. Also, and somewhat surprisingly, there is little impact of the vibration-translation energy transfer model, and a proper account for the vibrational relaxation time, easily achievable in the Larsen-Borgnakke model, appears to be sufficient. The lack of the VDF in the TCE model makes it poorly suited to computing gas relaxation at higher temperatures, although it is still acceptable for temperature below 5000K. Large overprediction of reaction rates in the QK model makes it a poor choice in practically all cases considered here. Reaction probability adjustment in QK makes it a much better model, as its accuracy then falls between the TCE and the Bias model, but such an adjustment defeats the QK purpose of being a parameter-free approach.

In oxygen-argon bath, the Bias model is shown to agree well with experimentally obtained vibrational temperature of O<sub>2</sub> and absorbance time histories, but there is some disagreement in the number densities of vibrational levels 4 and 6, which in part may be attributed to fill pressure uncertainties. For pure O<sub>2</sub> shocks, the absorbance time histories computed with the Bias mode are reasonably close to the measured values. However, the DSMC in this case overpredicts the maxima of vibrational temperature and densities of specific vibrational levels. Likely more important, the DSMC modeling predicts slower after-peak relaxation than the experiment; this could be due to differences in the O<sub>2</sub>-O dissociation rates, especially under non-equilibrium conditions. In air, DSMC predicts somewhat slower relaxation before the peak vibrational temperature, possibly due to inaccurate O<sub>2</sub>-N<sub>2</sub> V-T relaxation time, and, similar to pure O<sub>2</sub> cases, significantly slower relaxation after the peak. The latter could be attributed to Zeldovich reaction rates and non-equilibrium dissociation rates in O<sub>2</sub>-N<sub>2</sub> collisions. A multi-parametric study, ideally augmented by uncertainty quantification, might be necessary to pinpoint the actual reasons for the observed differences.

### 3. High Enthalpy Nozzle Flows

A fully kinetic, direct simulation Monte Carlo based approach is proposed to model a one-dimensional coreflow of high enthalpy nozzle expansion, and thus to estimate the impact of different non-equilibrium phenomena on gas properties at the nozzle exit. The approach can be used for any reservoir condition where the Boltzmann equation is applicable, and for any axially symmetric or two-dimensional nozzle geometry. The approach was verified versus analytical isentropic solutions for a diatomic gas with a constant specific heat ratio and companion axially symmetric Navier-Stokes solutions, and validated by comparing computational results with available DLR's L3K experimental data on plume expansion through a conical nozzle with a reservoir temperature of 5,100K.

The approach was then applied to flow and geometry conditions reproducing recent experiments in Caltech's T5 shock tunnel. Two vibration-translation and reaction models were used in order to evaluate the impact of thermal non-equilibrium model on air properties at the nozzle exit. In addition to the baseline excitation and reaction rates based on QCT results and shock tube data that became available in the last few years, the conventional set of reaction rate constants proposed by Park was used. Non-equilibrium real gas effect model was found to have little effect on the gas properties inside the nozzle under T5 conditions of reservoir pressure  $p_0=54$ MPa and temperature  $T_0=8348$ K. DSMC results are in good agreement with T5 measurements of nitric oxide density and internal temperatures, as well as flow velocity. The application of different rate constants provided an explanation for a published earlier significant discrepancy between the measured NO density and computed with Caltech's Navier-Stokes nozzle code. The reasons for the discrepancy are Zeldovich reaction rates and NO three-body recombination rates, and corrections to Park's recommended rate constants may be necessary.

Multi-parametric sensitivity studies have not provided a plausible explanation for significant drop in gas temperature at the nozzle exit recorded recently in T5 experiments. That drop was observed to exceed a factor of two over the duration of many high-enthalpy experimental shots, in all cases at a nearly flat, and sometimes even trending upward, nozzle-exit bulk flow velocity. The present computational study included the variation of all gas and numerical approach parameters and factors that were deemed to be relevant to the temperature decrease. Maximum temperature decrease obtained in the computations, with the constraints of decreasing reservoir pressure and constant nozzle-exit velocity, was 10%. The computations however were able to relate the decreasing reservoir pressure with significant decrease of nitric oxide density. Large sensitivity of results to reservoir temperature was shown, especially concentrations of primary observables, NO and O<sub>2</sub> species, which change by a factor of two at a 10% change of T<sub>0</sub>.

Computations were also conducted for nitrogen and air expansions through a conical nozzle of HEG shock tunnel experiments. At a similar reservoir pressure and 10% higher reservoir temperature, the HEG nozzle is significantly longer than in T5, thus providing much lower density, and also more non-equilibrium, conditions compared to T5. Computations indicate significant non-equilibrium between the nitrogen vibrational temperature and all other temperatures of internal and translational modes of air species (the difference between these other temperatures is negligible). Non-equilibrium collision models weakly impact bulk gas properties, with the vibration-dissociation coupling responsible for approximately 1-2% difference. That coupling has a large effect of the concentrations of NO and O<sub>2</sub>, increasing them by up to 50%.

#### **4. Ionized Flow Over Spacecraft**

Ionization of gas molecules and atoms in hypersonic non-equilibrium flow over spacecraft at high altitudes is well known to be important at reentry conditions when the free stream velocities exceed 10km/s, and the electron impact ionization significantly decreases gas temperatures and heat flux to the surface. At velocities below 6km/s, the gas temperature in the bow shock is known to be too low for ionization, and is usually neglected. This work is an attempt to examine the impact of ionization reactions on gas and surface properties in the intermediate flow regime, with free stream velocities ranging from 6 to 9km/s. Three air models were considered here, a 5 neutral species model, a 7 species model that adds NO<sup>+</sup> and e<sup>-</sup> produced in an associative ionization reaction between N and O, and a full 11 species model. The direct simulation Monte Carlo method was used in the computations, with all key thermal processes and neutral species reactions included. The ionization model validation was conducted for a one dimensional shock wave and an axially symmetric sphere-cone RAM-C geometry. RAM-C forebody was then used for the analysis of the model impact, with the Knudsen number varying between 0.0003 and 0.0012.

Comparison of computed peak electron number density in the shock layer with measured values showed an excellent agreement for the 11 species model, and an underprediction of that peak at Mach numbers M>20 for the 7 species model. Comparison of results obtained with the 5, 7, and 11 species models, and the model effect on the bulk flow, indicates that gas properties are nearly identical for the 7 and 11 species models inside the shock and in the hot layer between the shock and the boundary layer. The maximum translational temperatures are typically within one percent. There is significant difference, up to 80%, in gas density and temperature (but not pressure) near the wall for a free velocity of 9km/s. Comparison with the 5 species model shows that the peak translational temperature for the weakly ionized gas is visibly higher, increasing with flow velocity and reaching 10% at 9km/s. That difference also increases with gas density. Generally, the impact of ionization on the bulk gas properties in the shock region becomes significant at 9km/s, and in the boundary layer, at 8km/s. The 7 species model was shown to be a reasonable approximation to predict electron populations at velocities up to 7km/s. At 8km/s and 9km/s, it underpredicts peak electron densities by about 20% and 50%, respectively. The ionization impact on the heat flux is relatively minor, reaching about 4% for U=8km/s and Kn=0.0003. The 7 species model significantly, by up to a factor of two, underpredicts the heat flux reduction at U>8km/s.

All three models considered in this work have used standard reaction rate constants, and a separate study that performs a complete principal chemical reaction path analysis may still be needed to fully clarify the role of all the plasma reactions at different locations in the flow.

## 5. Oxygen Shock Wave

Experimental data of Ibraguimova et al on vibrational temperature of  $O_2$  in strong chemically reacting shock waves, inferred through time-dependent measurements of narrow-band absorption in the Schumann-Runge spectral range, have been revisited in this work. Detailed computational analysis of  $O_2$  shock waves at flow conditions matching the experiment is conducted through the statistical solution of the Boltzmann kinetic equation with the DSMC method. In order to minimize numerical uncertainties, accurate thermal and chemical relaxation models were used in these flow simulations, built to match results of the most recent available quasi-classical calculations of  $O_2$ - $O_2$  and  $O_2$ -O interactions. Spatially resolved translational temperature and rotational and vibrational level populations, obtained by DSMC, are then used to calculate absorption spectra. The detailed, quantum-state-based tool SPEKTR is applied for these cases, which calculates absorption from all rovibrational levels of the ground electronic state of  $O_2$  both for the bound-bound and bound-free transitions. It is the same tool that was used by Ibraguimova et al to estimate vibrational temperatures, although here it is applied in its forward, flow properties-to-absorption spectra, direction.

Comparison between the DSMC vibrational temperatures and those inferred by Ibraguimova et al is complemented by direct comparison between the measured and computed in-band absorption for shock velocities from 3.07 to 4.44km/s. For the higher velocity shock waves, the computed vibrational temperature has a significantly lower maximum, and somewhat different dissociation relaxation slope, as compared to that inferred from the experiment. However, the computed and measured time-dependent absorption profiles are much closer, with excellent agreement near the peak, and very similar slopes in the dissociation relaxation zone. Numerical analysis conducted based on the actual non-equilibrium rovibrational populations, and the corresponding 2-T Boltzmann ones, indicates that one possible reason for the disagreement in the maximum vibrational temperature could be the two-temperature assumption that Ibraguimova et al had to use in their work. For the lower-velocity shock waves, the numerical results agree reasonably well with the measurements near the peak vibrational temperature, where the absorption is maximum. Further downstream, in the dissociation relaxation zone, there is significant difference. The computed absorption, as well as vibrational temperature, decrease much more gradually than those observed in the experiments. The reasons for that difference are still to be found, and may lie in the shock wave signal being recorded during significant downward change of the lamp signal. It may also be related to the merging of the after-shock dissociation relaxation zone with the contact discontinuity zone, which thickness becomes substantial for the relatively low temperature conditions of the 3.07km/s shock wave. Generally, the work provides an indication that direct comparison of computed and measured absorption signals may offer better insight, and a better validation platform, than comparing vibrational temperatures.

## 6. Recombination Reactions

The direct simulation Monte Carlo method was used in this work to examine the effect of gas-phase recombination reactions on aerothermodynamic and gas properties in hypersonic near-continuum flow over a cylinder. Only nitrogen recombination that occurs in the vicinity of the wall was found to be important. Such recombination dominates the heat flux, almost doubling its maximum value at the stagnation point for the baseline conditions. Its impact on skin friction is much smaller, but still noticeable, thus indicating that accurate modeling of  $N+N$  recombination is critical for both thermal properties and aerodynamics.

Variation of free stream properties have shown that the effect of nitrogen recombination in the gas phase increases with the free stream velocity and density, and is most significant at the stagnation point, where the maximum heating is observed. Analysis of result sensitivity to nitrogen recombination rate have shown moderate impact at lower densities. Changing models of molecular dissociation and vibrational energy transfer has practically no impact on results likely due to the dominant role of molecule-atom interactions, primarily  $N_2$ -O. Surface temperature was found to be very important, as the heat flux to the wall added due to gas recombination becomes smaller for higher wall temperatures. Still, even for a wall temperature of 2000K the nitrogen recombination was responsible for as much as 20% of the total heat flux to the wall in the stagnation region.

## Publications

Gimelshein, S.F., Streicher, J., Krish, A., Hanson, R., Wysong, I., Application of Reflected Shock Wave Configuration to Validate Nonequilibrium Models of Reacting Air, submitted to *Physics of Fluids* January 2022.

Gimelshein, S. F., & Wysong, I. J. (2021). Nonequilibrium effects in high enthalpy gas flows expanding through nozzles. *Physics of Fluids*, 33(10), 106104. <https://doi.org/10.1063/5.0068917>

Gimelshein, S.F., Wysong, I.J., Fangman, A.J., Andrienko, D.A. et al (2021) Kinetic and Continuum Modeling of High Temperature Air Relaxation, Submitted to *J. Thermophysics and Heat Transfer*, July 2021.

Gimelshein, S.F., Wysong, I.J., Fangman, A.J., Andrienko, D.A. et al (2021) Kinetic and Continuum Modeling of High Temperature Relaxation of O<sub>2</sub> and N<sub>2</sub> Binary Mixtures, *J. Thermophysics and Heat Transfer*, published online 20 Dec 2021. <https://doi.org/10.2514/1.T6258>

Gimelshein, S.F. (2021), Particle Modeling of Reflected Shock Waves, *J. Thermophysics and Heat Transfer*, Volume 35, Number 2, April 2021. <https://doi.org/10.2514/1.T6103>

Gimelshein, S.F., Wysong, I.J. (2020). Impact of the ionization reaction set in nonequilibrium hypersonic air flows. *AIAA Journal*, 58(3), 1255-1265. <https://doi.org/10.2514/1.J058895>

Gimelshein, S. F., Wysong, I. J., Bykova, N. G., Shatalov, O. P., & Zabelinskii, I. E. (2020). Improved Analysis of O<sub>2</sub> Ultraviolet Absorption Spectra Under Nonequilibrium Shock Conditions. *AIAA Journal*, 1-10. <https://doi.org/10.2514/1.J058961>

Gimelshein, S.F., Wysong, I.J. (2020), Applicability of 5, 7, and 11 Species Air Models in Nonequilibrium Hypersonic Reacting Flows, *AIAA* 2020-2190. <https://doi.org/10.2514/6.2020-2190>

Gimelshein, S. F., & Wysong, I. J., Bird's chemistry model for given reaction rates: 4 decades and going strong, *Physics of Fluids*, Vol. 31, No. 7, 2019. <https://doi.org/10.1063/1.5097706> PA19168

Gimelshein, S. F., & Wysong, I. J. (2019). Gas-phase recombination effect on surface heating in nonequilibrium hypersonic flows. *Journal of Thermophysics and Heat Transfer*, 33(3), 638-646. <https://doi.org/10.2514/1.T5556>

## List of Symbols, Abbreviations, and Acronyms

AFOSR	Air Force Office of Scientific Research
CFD	Computational Fluid Dynamics
DSMC	Direct Simulation Monte Carlo
FHO	Forced Harmonic Oscillator
FR	Free-rotation
HEG	High Enthalpy Shock Tunnel Gottingen
HyNECC	Hypersonic Non-Equilibrium Comparison Cases
IR	Infrared
MMT	Modified Marrone-Treanor
NO	Nitric Oxide
NS	Navier-Stokes
QCT	Quasi-Classical Trajectory
QK	Quantum Kinetic
QK	Quantum Kinetic
TCE	Total Collision Energy
UV	Ultraviolet
VDF	Vibrational Distribution Function
V-T	vibration-translation
V-V	vibration-vibration