

DSMC Predictions of Non-equilibrium Reaction Rates

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Abstract. A set of Direct Simulation Monte Carlo (DSMC) chemical-reaction models recently proposed by Bird and based solely on the collision energy and the vibrational energy levels of the species involved is applied to calculate non-equilibrium chemical-reaction rates for atmospheric reactions in hypersonic flows. The DSMC non-equilibrium model predictions are in good agreement with theoretical models and experimental measurements. The observed agreement provides strong evidence that modeling chemical reactions using only the collision energy and the vibrational energy levels provides an accurate method for predicting non-equilibrium chemical-reaction rates.

Keywords: Direct Simulation Monte Carlo, hypersonic flow, atmospheric chemistry, non-equilibrium rates

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INTRODUCTION

Although the problem of calculating chemically reacting flow fields in the rarefied hypersonic regime has been studied since the Apollo era [1], an understanding of the influence of thermal non-equilibrium on atmospheric reaction rates still remains elusive. Multiple theoretical and empirical methods have been proposed that aim to capture the impact of non-equilibrium energy distribution between the available energy modes on chemical reaction rates [2]. A common issue with these models is that they rely on experimental data taken at conditions that do not match the flight environment and therefore employ empirical fits extrapolated to flight conditions.

Bird recently proposed [3] new types of chemical reaction models for the Direct Simulation Monte Carlo (DSMC) method [4] based solely on properties of the colliding molecules and that do not use measured equilibrium reaction rates or any adjustable parameters. The microscopic properties used in these models include the available collision energy, dissociation energies, and quantized vibrational energy levels. These DSMC models link the chemical-reaction process to the energy content of the vibrational modes of the colliding molecules. Application of chemical-reaction procedures for collisions between molecules that could lead to endothermic reactions is conceptually straightforward. The models for these “forward” endothermic reactions and the principle of microscopic reversibility are then used to develop models for the corresponding “reverse” exothermic reactions. These models satisfy microscopic reversibility by balancing the fluxes into and out of each state and do not require any macroscopic rate information.

The lack of adjustable parameters means that these models cannot be calibrated to reproduce a given equilibrium reaction rate. Instead, the new models predict reaction rates, even for thermal equilibrium conditions. For dissociation, ionization, and exchange reaction types, the DSMC models produce equilibrium reaction rates that are in good qualitative and quantitative agreement with the best available theoretical and measured or extrapolated reaction rates [5]. The differences between the most reliable reaction rates and the corresponding DSMC values are usually less than an order of magnitude, which typically is comparable to the uncertainties in measurements.

Besides their conceptual simplicity and their ability to reproduce known rates, the most significant advantage of these models is that they do not rely on macroscopic, experimentally-measured reaction rates. The fact that these models are implemented in an inherently non-equilibrium method like DSMC suggests that non-equilibrium chemical-reaction rates can be calculated with reasonable accuracy. This feature of the new models can be particularly important in cases where even the equilibrium reaction rates are not known.

NON-EQUILIBRIUM RATES FOR ATMOSPHERIC REACTIONS

The ability of a chemistry model to reproduce equilibrium chemical reaction rates is a necessary condition to simulate chemically reacting flows. However, in atmospheric hypersonic flows, the chemical reactions take place under non-equilibrium conditions. Thus, accurate prediction of chemical reaction rates under non-equilibrium conditions is also important.

Measurements of internal-energy-dependent cross sections of reactions between atmospheric species are extremely rare [6,7]. Some systematic measurements and calculations exist for molecular hydrogen, where the cross section is found to be significantly affected by the distribution of energy among the reactant molecules. However, due to the relatively more important role of quantum effects in its interactions, the behavior of hydrogen is expected to deviate from the behavior of heavier, and therefore more classical, atmospheric molecules.

In the absence of detailed state-specific information that can be used to validate models for non-equilibrium conditions, a comprehensive evaluation of any state-specific chemistry model is not possible. Therefore, the DSMC chemistry models are herein compared to non-equilibrium chemical reaction rates from approximate empirical and theoretical models. Although comparisons with more established theoretical models cannot provide validations of the DSMC models, they offer insight into the performance of these models under non-equilibrium conditions.

Using the DSMC chemistry models, arbitrary non-equilibrium conditions can be simulated, and the effective reaction rate under non-equilibrium conditions can be calculated. Calculating non-equilibrium reaction rates with the DSMC models presented herein entails no differences in modeling since only collision-energy and vibrational-energy-level information is used. For the DSMC rates calculated herein, 10^6 molecule-simulators were used in a single-cell DSMC code. Each calculation was completed when approximately 10^6 successful events were observed.

Comparison with Measured Non-equilibrium Reaction Rates

Very limited data are available for atmospheric reaction rates under non-equilibrium conditions. Sergievskaya et al. [8] report the upper and lower limits of measurements of a small number of dissociation reaction rates obtained from shock-tube measurements that involve atmospheric oxygen. In these experiments, the vibrational temperature was constant at 4,200 K, and the translational and rotational temperatures were kept in equilibrium with each other. The non-equilibrium rates are presented in terms of the deviational parameter

$$Z(T_{tr}, T_{vib}) = k(T_{tr}, T_{vib}) / k(T), \quad (1)$$

where T_{tr} , T_{vib} , and T are the translational, vibrational, and equilibrium temperatures, respectively, and k is the reaction rate.

The measured rates are compared to DSMC predictions in Figure 1. For a translational temperature of 4,200 K, measured and predicted rates are equal. For these conditions, the gas is in thermal equilibrium, so the deviational parameter equals unity. As the translational temperature increases, the degree of non-equilibrium also increases. An indication of the measurement uncertainty is given by the underprediction of the equilibrium point, where the upper bound of the measurements is at the expected value of unity but the lower bound is significantly different. As conditions depart from equilibrium, the DSMC rates lie within the experimental bounds, with the exception of the point at 10,000 K, where the DSMC model slightly overpredicts the experimental value. This overprediction is less than the uncertainty in the measurements near the equilibrium point and is much less than the difference between the lower and upper bounds at 10,000 K. Although not quite one order of magnitude, the spread in the experimental measurements is significant, so an unequivocal assessment of the models cannot be made.

Comparison with Theoretical and Empirical Non-equilibrium Models

Significant effort has been expended in theoretical attempts to express the dependence of the reaction rate on the degree of vibrational excitation. Many empirical and theoretical models [2] have been proposed for the non-equilibrium deviational parameter $Z(T_{tr}, T_{vib})$ of Equation (1). Some of these models use empirical or adjustable parameters that are estimated based on experimental data or quantum mechanical computations, and some require only microscopic information. The existing empirical and theoretical models for dissociation reactions are more

advanced than those for exchange reactions. Both classes of models have been extensively reviewed in the literature [2 and references therein].

As a first approach to theoretically study chemical reactions under conditions of non-equilibrium, the vibrational temperature can be prescribed independently from the temperature of the translational and rotational modes. Thus, the gas is characterized by two temperatures: T_{tr} , which describes the translational and rotational modes, and T_{vib} , which describes the vibrational mode. Thus, the energy states are distributed according to the Boltzmann distribution for the internal modes and the Maxwell distribution for the translational modes. To some degree, these conditions represent the state of a gas in a Navier-Stokes non-equilibrium calculation.

Dissociation Reactions

For dissociation reactions and for the particular situation of the translational and vibrational energies being distributed according to their equilibrium distributions but at different translational and vibrational temperatures (T_{tr} and T_{vib} , respectively), the reaction rate can be analytically calculated as

$$k(T_{tr}, T_{vib}) = \frac{2\sigma_{ref}}{\varepsilon\sqrt{\pi}} \left(\frac{T_{tr}}{T_{ref}}\right)^{1-\omega} \left(\frac{2k_B T_{ref}}{m_r}\right)^{1/2} \left\{ \sum_{i=0}^{i_d} Q \left[\frac{5}{2} - \omega, \frac{\Theta_d - (i-1)\Theta_v}{T_{tr}} \right] \frac{\exp[-i\Theta_v/T_{vib}]}{z_{vib}(T_{vib})} + B \sum_{i=i_d+1}^{\infty} \frac{\exp[-i\Theta_v/T_{vib}]}{z_{vib}(T_{vib})} \right\}, \quad (2)$$

where $Q[5/2 - \omega, (\Theta_d - (i-1)\Theta_v)/T] = \Gamma[5/2 - \omega, (\Theta_d - i\Theta_v)/T] / \Gamma[5/2 - \omega]$ is the probability of the translational energy exceeding the difference between the level i and the dissociation level i_d , $z_{vib} = (1 - \exp[-\Theta_v/T])^{-1}$ is the vibrational partition function in the harmonic oscillator model, σ , ω , and m_r are the collision cross section, viscosity temperature exponent, and reduced mass of the pair, respectively, ε is a symmetry parameter that is set to 1 for like molecules and to 2 for unlike molecules, and Γ is the incomplete gamma function. The parameter B takes the values of 0 or 1 depending on whether the harmonic oscillator model for the vibrational states is truncated at the dissociation level or is not truncated.

Figure 2 presents analytical and numerical predictions of non-equilibrium reaction rates for oxygen dissociation using the model of Equation (2). The non-equilibrium reaction rates are given as a function of the vibrational temperature at translational-rotational temperatures of 15,000 K, 10,000 K, 5,000 K, and 3,000 K. The vibrational energy is distributed according to the harmonic oscillator model at temperatures from 500 K to 15,000 K. The values from Equation (2) are designated by curves, whereas the numerically calculated values are designated by symbols. As observed for equilibrium conditions [5], the numerical values are in good agreement with the analytical expression for non-equilibrium conditions, indicating that the DSMC model is correctly implemented.

In agreement with theoretical predictions and experimental evidence [2,9], the new DSMC model predicts that the role of the vibrational energy in promoting a reaction varies with total energy available for a particular reaction. The energy requirements of reactions become less restrictive at higher collision energies. At low collision energies, the selective energy requirements can significantly influence the reaction rate. This behavior has been commonly observed [9] for the particular case of dissociation reactions, where higher vibrational temperatures become particularly effective in promoting dissociation reactions.

Figure 3 compares oxygen dissociation rates from the DSMC model and the Adiabatic Dissociation Model (ADM) of Smekhov et al. (in Chernyi et al. [2]) for translational-rotational temperatures of 15,000 K, 10,000 K, 5,000 K, and 3,000 K. The ADM model is one of the most general models for dissociation reactions and is based entirely on theoretical considerations. The ADM model assumes that the energy states are distributed according to the Boltzmann distribution for the vibrational modes and the Maxwell distribution for the translational modes. The vibrational and translational modes are each characterized by single but distinct temperatures. The ADM model assumes that dissociation can occur from any vibrational level, including the ground state. However, the energy threshold is a function of the translational energy, which accounts for intra-molecular energy transfer during a collision. The dissociation cross section is given by the Massey adiabatic parameter as $\sigma = \sigma_T \exp(-\xi)$, where σ_T is the total cross section and ξ is a function of the translational energy (Chernyi et al. [2]). The vibrational mode is described by the Morse anharmonic oscillator model. The DSMC rates are in excellent agreement with the ADM rates, especially for low temperatures. The slight degradation of agreement for higher temperatures can be attributed to the harmonic oscillator model used in the DSMC model to describe the vibrational mode.

Figure 4 presents oxygen dissociation rates from the DSMC model and the Treanor-Marrone (T-M) model [1]. The T-M model uses a truncated harmonic oscillator to describe the vibrational mode and assumes that dissociation can occur from any vibrational state without distorting the Boltzmann distribution of molecules over vibrational levels. The T-M model contains an adjustable parameter that is estimated from experimental data or quantum mechanical calculations. The value suggested by Chernyi et al. [2] is used here. According to Capitelli et al. [10], this adjustable parameter must depend on the translational temperature and on the vibrational level for the T-M model to agree with quantum mechanical calculations, and, even when these dependences are included, the T-M model underpredicts reaction rates for low vibrational temperatures. These observations may explain why the T-M rates lie below the DSMC rates, especially at low temperatures. The differences between the ADM, T-M, and DSMC models are attributed to differences in how each model allows translational energy to promote dissociation reactions from low vibrational states.

The DSMC model is in reasonable quantitative agreement with all of these theoretical models for high collision energies. Good agreement is also observed between the DSMC model and the ADM model for low vibrational temperatures, where the reaction rate is influenced mainly by the translational energy of the colliding pair. The qualitative agreement between the various models indicates that all of these models are predicting similar reaction energy selectivity. More importantly, the DSMC model and all theoretical models predict non-vanishing reaction rates as the vibrational temperature tends to zero. The large differences between the ADM and T-M models in this limit may be taken as an indication of the uncertainty in these theoretical models. In the light of this, the qualitative agreement cannot lead to an unequivocal assessment of the accuracy of any of these models. These conclusions are not unique to oxygen dissociation. Results have also been obtained for nitrogen dissociation but are not presented here since they are qualitatively similar to the results obtained for oxygen dissociation.

Exchange Reactions

Figure 5 and Figure 6 compare the DSMC model and the α model of Rusanov and Fridman (Chernyi et al. [2]) for the endothermic exchange reactions $N_2 + O \rightarrow NO + N$ and $NO + O \rightarrow O_2 + N$. The α model assumes that only a fraction α of the vibrational energy participates in overcoming the energy threshold, whereas the translational energy is fully utilized in overcoming the energy threshold. The DSMC model produces non-equilibrium reaction rates that are in good agreement with non-equilibrium rates from the α model. This agreement cannot be considered a validation of either of the two models since they both are theoretically based. The fraction α of the vibrational energy that participates in overcoming the energy threshold in addition to the translational energy is judiciously picked and could be related to the average vibrational energy that is disposed to the vibrational mode of the potentially formed products of the reaction. Chernyi et al. [2] give values of $\alpha = 0.51$ and $\alpha = 0.94$ for the two reactions but also point out that α is expected to be in the interval $0.9 \leq \alpha \leq 1.0$ for endothermic reactions. This may be the reason that the α model agrees more closely with DSMC for the reaction $NO + O \rightarrow O_2 + N$, where $\alpha = 0.94$, than for the reaction $N_2 + O \rightarrow NO + N$, where $\alpha = 0.51$.

The DSMC and α models are in good agreement in the low-vibrational-temperature regime because both models allow the translational energy alone to be used to overcome the energy threshold of the reaction. Unlike the DSMC model for dissociation reactions, the DSMC model for exchange reactions considers post-collision properties of the colliding molecules. While the post-collision distribution of energy is known under equilibrium conditions, it is not known under non-equilibrium conditions. Thus, an analytical expression similar to that of Equation (2) for exchange reactions cannot be derived under non-equilibrium conditions. However, close examination of the non-equilibrium DSMC reaction rates indicates that both reactions can be fit with an expression of the form

$$k(T_{tr}, T_{vib}) = c_1 k_{eq}(T_{tr}) + c_2 k_{eq}(T_{vib}) + (1 - c_1 - c_2) k_{eq}(T_{av}) \quad (3)$$

using the same values for the two dimensionless parameters c_1 and c_2 , where k_{eq} is the equilibrium reaction rate as given by Bird [3] and T_{av} is the average temperature.

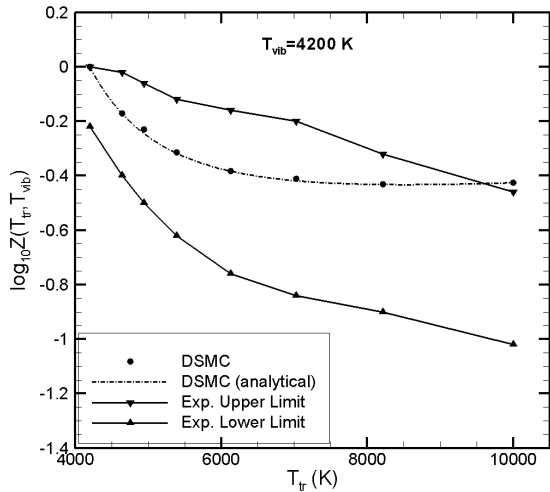


FIGURE 1. DSMC and measured non-equilibrium rates.

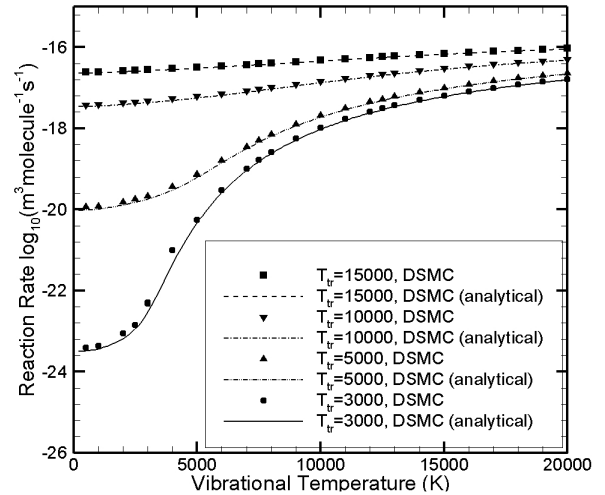


FIGURE 2. DSMC numerical and analytical results for non-equilibrium conditions.

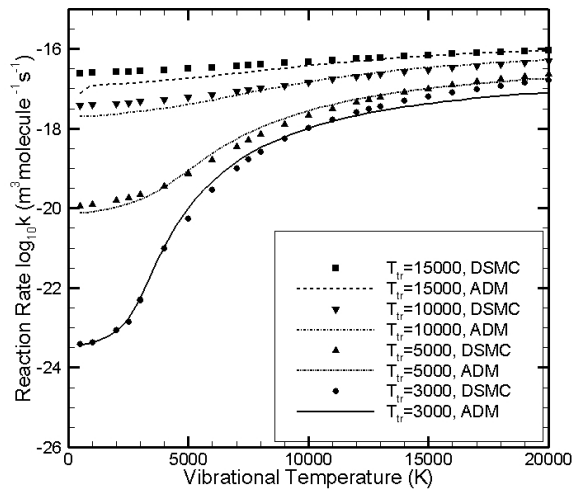


FIGURE 3. DSMC and the ADM model.

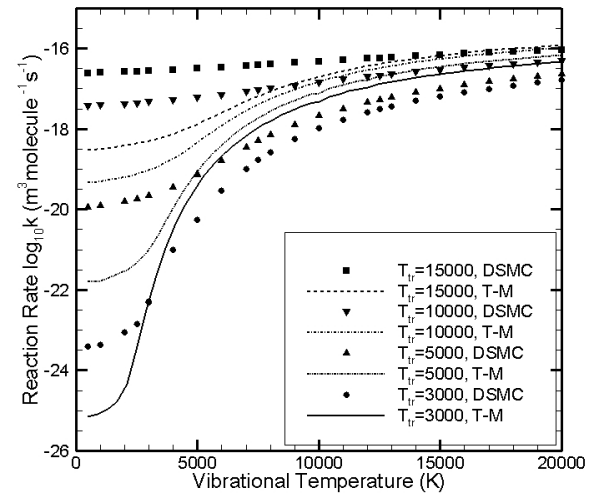


FIGURE 4. DSMC and the Treanor-Marrone model.

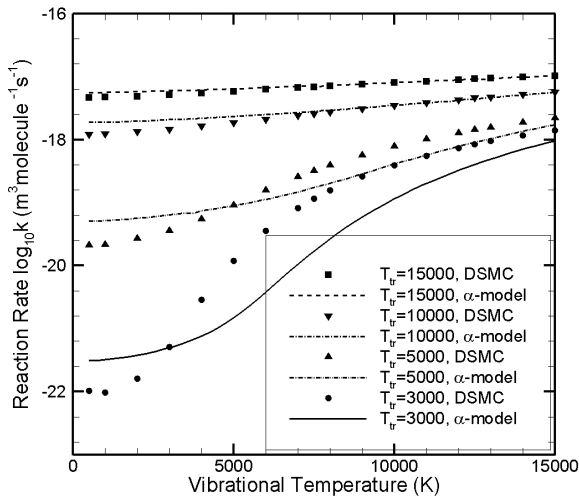


FIGURE 5. $N_2 + O \rightarrow NO + N$ exchange reaction. DSMC and the α model.

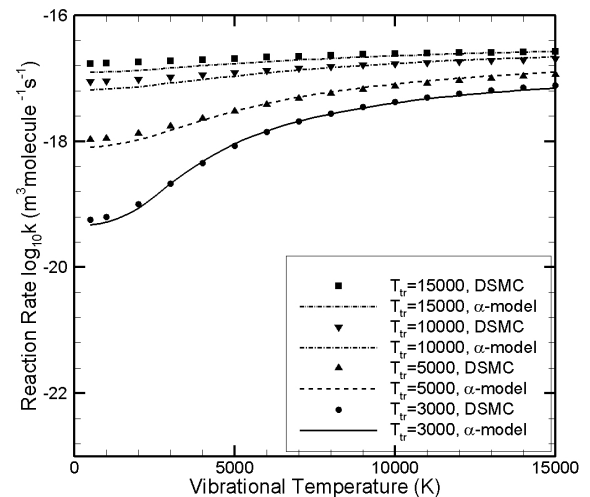


FIGURE 6. $NO + O \rightarrow O_2 + N$ exchange reaction. DSMC and the α model.

CONCLUSIONS

For non-equilibrium conditions, the DSMC chemistry models produce reaction rates that are in good qualitative and quantitative agreement with theoretical models and that lie within the accuracy of measured non-equilibrium reaction rates. In agreement with theoretical predictions and experimental observations, the DSMC results indicate that the dependence of a reaction rate on the distribution of the reactant energy among the available modes diminishes as the total collision energy increases.

Currently, the ability to simulate upper-atmosphere hypersonic flows and environments is hampered by using chemical-reaction-rate models of unknown accuracy that introduce unknown errors into calculations. The new DSMC models lead to a predictive and self-consistent capability for determining equilibrium and non-equilibrium chemical-reaction rates that does not rely on measured equilibrium rates. The new models also simplify validation and uncertainty quantification relative to empirical models because they use no adjustable parameters.

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