DSMC Simulation of Entry Vehicle Flowfields Using a Collision-Based Chemical Kinetics Approach

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Abstract. A study of high-altitude, nonequilibrium flows about an Orion Command Module (CM) is conducted using the collision-based chemical kinetics approach introduced by Bird in 2008. DSMC simulations are performed for Earth entry flow conditions and show significant differences in molecular dissociation in the shock layer from those obtained using traditional temperature-based procedures with an attendant reduction in the surface heat flux. Reaction rates derived from equilibrium simulations are also presented for selected reactions relevant to entry flow kinetics, and comparisons to various experimental and theoretical results are presented.

Keywords: DSMC, Entry flows, Nonequilibrium flows, Chemical Kinetics
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INTRODUCTION

Bird introduced a new collision-based chemical kinetics approach in 2008 [1] in which reactions can be modeled without dependence on local macroscopic properties. This new approach has been shown to produce equilibrium reaction rates that are in good agreement with those derived from experiment for dissociation, recombination and exchange reactions [1-2]. In the new approach, these particular types of reactions are determined to proceed based only on the total collision energy, molecular vibrational energy and molecular dissociation energy. Macroscopic reaction rates which have traditionally been used to calculate reaction probabilities in DSMC [3] based on kinetic theory of bimolecular and termolecular reactions are no longer needed in the new method. Therefore, DSMC simulations which use the new kinetics approach are expected to be more accurate in regions of highly nonequilibrium flow where Boltzmann velocity and energy distributions may not be applicable.

In the present study, DSMC simulations are performed using both the new collision-based kinetics model and the traditional temperature-based rate model for an Orion command module at entry conditions selected from those analyzed by Moss, et. al., [4]. Comparisons of flowfield and surface properties obtained with the two kinetics models are examined. Simulations with both models are performed using Bird's DS2V program [5], while additional simulations with the traditional temperature-based kinetics model are performed using the DAC program [6]. Vibrational relaxation rates are computed based on a quantized collision temperature using the empirical relaxation expression suggested by Bird [1] with parameters determined from a generalized experimental curve fit from Millikan and White [7].

In addition to entry flow simulations, equilibrium reaction rate predictions similar to those presented in Refs. 1-2 are examined to provide an assessment of the new kinetics approach for modeling additional species and reactions needed for various planetary entry simulations. The additional species include polyatomic molecules such as carbon dioxide which have multiple vibrational modes that must be considered within the context of the new approach. Various detailed-balance methodologies are considered including those suggested by Bird [1] for treating recombination and exchange reactions which appear to provide reasonable predictions of equilibrium composition for air at various temperatures.

DSMC SIMULATIONS

DSMC simulations were performed for two of the freestream conditions used by Moss in studies of the aerothermodynamics of the Orion command model [4] and are presented in TABLE 1. All simulations were performed at a freestream velocity of 7.6 km/s with the wall collisions treated as fully diffuse scattering and accommodated to the radiative equilibrium wall temperature. Simulations were performed using the DS2V program of Bird [5] with both the traditional rate-based methodology (referred to as the "old chemistry") and the new collision-based methodology (referred to as the "new chemistry"). Unfortunately, the version of DS2V available at the time the simulations were performed did not have the new models for exchange and recombination implemented. Therefore, all exchange and recombination reactions were treated with the traditional rate-based methods and only the dissociation reactions were treated with the new collision-based method so that the "new chemistry" used here was actually a mixture of old and new methodologies. However, additional simulations were performed in which the exchange and recombination reactions were completely ignored, i.e., only dissociation modeled, and comparisons with results obtained when the full set of reactions was used showed that, at the altitudes studied here, the exchange and recombination played a negligible role in the prediction of flowfield and surface properties. Simulations with the DAC code were performed only using the old chemistry mainly to provide verification of the surface results.

TABLE 1. Freestream conditions for the simulations

			Mole fractions			
Altitude, km	**Number density, 1/m^3**	**Temperature, K**	**O_2**	**N_2**	**O**	**T_{wall}, K**
105	4.98×10^{18}	211	0.1528	0.7819	0.0653	760
95	2.90×10^{19}	189	0.1972	0.7869	0.0159	951

The new chemistry also uses a new expression to describe the vibrational relaxation collision number, Z_v, as a function of temperature [1]. Note that although this relation is expressed in terms of temperature, the value used in the simulations is a quantized collision temperature which is based on the integer value of the ratio of the total collision energy to the characteristic vibrational energy. This new expression provides for specification of Z_v at two different temperatures with one of those recommended to be $Z_v = 1$ at the temperature corresponding to the dissociation energy and the second specification to be at an appropriate reference temperature. In the present study, the reference temperature was chosen to be the characteristic vibrational temperature and $Z_{v,ref}$ chosen to match the generalized curve fit for the vibrational relaxation time given by Millikan and White [7]. Since the vibrational collision number, Z_v, is just the product of the collision rate and the relaxation time, the Millikan-White curve fit was used to calculate Z_v at the appropriate reference temperature for different collision partners, and the results for the species of interest to the entry flow simulations are given in TABLE 2.

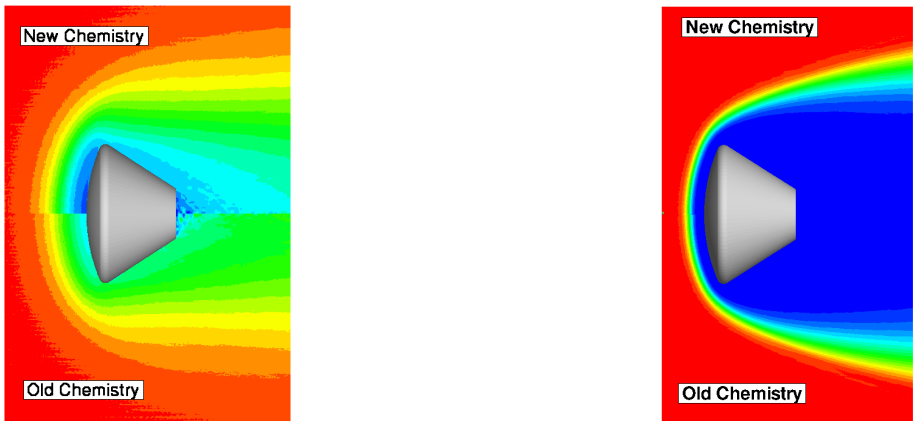
TABLE 2. Vibrational relaxation collision number at the characteristic vibrational temperature based on Millikan-White data

Vibrator	**Collision Partner**	**Temperature, K**	**$Z_{v,ref}$**
N_2	N_2	3371	58390
N_2	O_2	3371	62596
N_2	NO	3371	59173
N_2	N	3371	17749
N_2	O	3371	21045
O_2	N_2	2256	9132
O_2	O_2	2256	9659
O_2	NO	2256	9253
O_2	N	2256	3263
O_2	O	2256	3729
NO	N_2	2719	19956
NO	O_2	2719	21265
NO	NO	2719	20230
NO	N	2719	6618
NO	O	2719	7696

RESULTS

Orion Entry Simulations

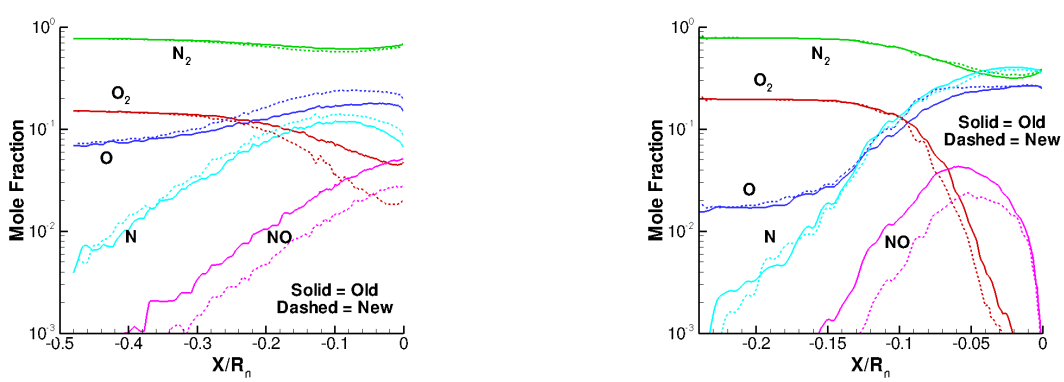
FIGURE 1 shows comparisons of mole fractions of molecular oxygen for the two altitudes studied. Oxygen behavior is highlighted here because equilibrium dissociation rate calculations with the new collision-based approach show surprisingly good agreement with the macroscopic rates for oxygen. Therefore, any differences between the results shown in FIGURE 1 obtained with the new and old chemistry should highlight nonequilibrium effects on the chemical kinetics. At 105 km, the flow is more rarefied with a thicker more diffuse shock layer than at 95 km, and significant differences in the level of dissociation are evident between the two methods. With the new chemistry, oxygen dissociation at 105 km occurs earlier (farther from the body) and is nearly complete near the forebody wall. At 95 km, the qualitative differences are much less evident, and both methods produce nearly complete dissociation behind the shock.



(a) 105 km. **(b)** 95 km.

FIGURE 1. Comparisons of O_2 mole fraction contours for Orion command module.

Mole fractions of all five species are shown along a stagnation line in FIGURE 2. Nitrogen dissociation is much less pronounced than oxygen dissociation because of its higher dissociation energy. The differences in oxygen dissociation and the corresponding increase in atomic oxygen levels obtained with the old and new chemistry are more pronounced at 105 km than at 95 km. Although differences in O_2 levels between old and new chemistry results are evident inside the shock layer at 95 km, both methods produce almost complete dissociation near the forebody surface. Differences in NO production are also apparent between the two methods. It should be noted that

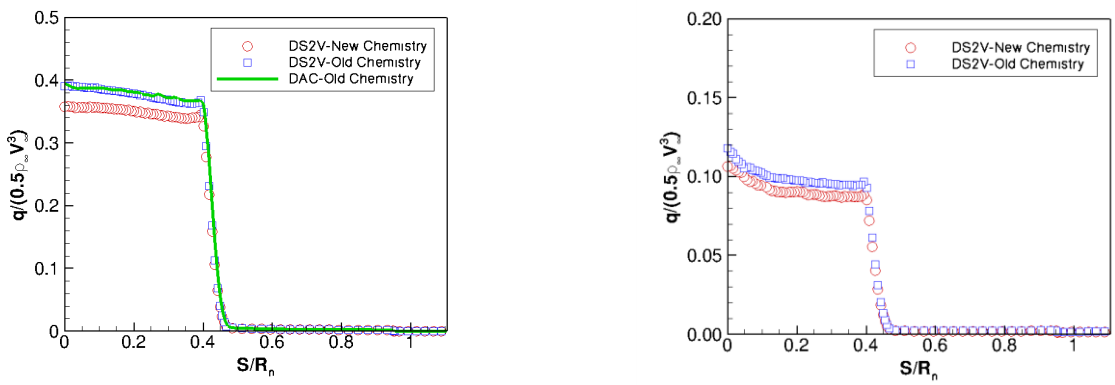


(a) 105 km. **(b)** 95 km.

FIGURE 2. Comparisons of mole fractions for molecular and atomic species along the stagnation line.

NO is produced primarily through the endothermic exchange reactions, N_2+O→NO and O_2+N→NO, which in the present study were modeled using the old chemistry for all DSMC runs. Therefore, further studies are needed in which the collision-based methodology is used for all reactions to ensure that the observed NO behavior is not an artifact of using mixed methodologies. However, auxiliary simulations, in which exchange and recombination reactions were ignored, i.e., only dissociation was considered, were performed for the 105 km flow conditions, and the dissociation levels for oxygen and nitrogen were found to be essentially the same as those shown in FIGURE 2. Furthermore, neglecting these reactions was found to have a negligible effect on the overall energetics of the shock layer and the resulting surface pressure and heating at the higher altitude.

Surface heating properties obtained with the two chemistry models are shown in FIGURE 3. For the 105 km case, results from a DAC simulation which used the old chemistry model are shown for comparison and agree quite well with the DS2V result that used the same model. The forebody heating rate predicted using the new chemistry is nominally 8-10 percent lower than that with the old chemistry for both altitudes, although the non-dimensionalized differences are much lower for 95 km than for 105 km. This result is difficult to interpret in regard to the 95 km case, since the differences in the dissociation predicted with the two methods appear to be much smaller than those for the 105 km case. It is worth noting that the computational figure of merit recommended by Bird for DS2V calculations which is the ratio of the mean collision separation (*mcs*) to the mean free path (*mfp*) is much higher for the 95 km result although it is still within acceptable limits. For both cases, the largest values for this ratio (*mcs/mfp*) occur near the forebody wall, and for 105 km, $(mcs/mfp)_{max}$=0.1 while for 95 km, $(mcs/mfp)_{max}$=0.5. Since the heating rate is computed from the difference of the sampled incident and reflected energy, it is more sensitive to cell resolution near the wall than other quantities such as pressure. For the current cases, there were negligible differences in the pressure between the new and old chemistry for either altitude.



(a) 105 km. **(b)** 95 km.

FIGURE 3. Comparisons of surface heating rates.

Equilibrium Rate Predictions

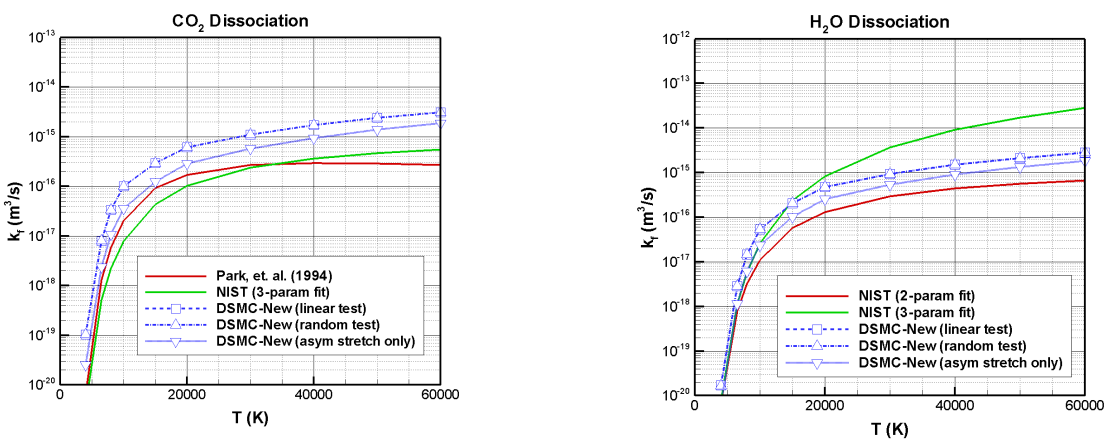
Although the primary benefits of the collision-based chemistry model are expected to be obtained under highly-nonequilibrium conditions, it is important that the model also produce valid results under equilibrium conditions. Equilibrium rate predictions for dissociation, exchange, and recombination reactions commonly used to model high-temperature air kinetics for entry flow simulations have been evaluated using the new quantum, collision-based methodologies [1-2], and comparisons with experimental and theoretical rates show agreement that is generally within the estimated uncertainties. Similar comparisons were made in the current study using a simple DSMC program in which the new chemistry model was implemented for a zero-dimensional, single cell having a unit volume of one cubic meter. Comparisons were made to the results in Ref. [2] for the same air species and reactions, and the current study produced results that are essentially identical to those in Ref. [2], since both studies used essentially the same variable hard sphere collision parameters and the same Larsen-Borgankke procedures as those in DS2V.

All of the species and reactions examined to date with the new chemistry have only considered diatomic and monatomic species, so that only a single characteristic vibrational model needed to be considered. In the present work, preliminary assessments have begun in which the same procedures are applied to the polyatomic species, CO_2

and H_2O. CO_2 represents a class of molecules having a linear, triatomic geometry while H_2O has an angular or bent geometry. Therefore, CO_2 has vibrational modes that represent bending and symmetric and asymmetric stretching where the bending mode has a degeneracy of two, so a total of four characteristic modes should be considered. H_2O represents a nonlinear or bent geometry, so that only three modes need be considered. Although anharmonic effects are likely to be more important for these various modes, especially at high temperatures, our initial assessments treated each of these modes as a simple harmonic oscillator. Furthermore, it is not clear that all modes should be treated equally with respect to dissociation. Since modal and rotational coupling effects are ignored, comparisons are also made using different methodologies for examining the modes to determine whether dissociation occurs.

Results from simulations of CO_2 dissociation ($CO_2 \rightarrow CO+O$) and H_2O dissociation ($H_2O \rightarrow OH+O$) are shown in FIGURE 4. For the first two DSMC simulations (labeled linear test and random test), dissociation was assumed to occur when the vibrational energy of any mode exceeded the dissociation energy. To determine if the order in which the modes were tested might bias the results, runs were performed in which the modes were examined sequentially (linear) and in which the modes were examined randomly, and no significant difference was found. Simulations were also performed where only the asymmetric stretch mode was examined, and this simulation produced rates that were lower by a factor of about 2.5. Comparisons of CO_2 predictions are made to the empirical curve fit of Park, et.al., [8] and to a three-parameter curve fit to data in the NIST chemical kinetics database [9]. All three DSMC approaches produced rates that were higher than either the Park or the NIST data but were generally within a factor of ten for temperature ranges less than about 50,000 K.

H_2O simulations gave dissociation rates that were higher than the NIST 3-parameter curve fit at lower temperatures but fell below the 3-parameter curve at higher temperatures. However, the NIST data given for H_2O were for second-order reactions which are more accurately described by a two-parameter curve fit. The DSMC results fall between these two curve fits at higher temperatures. As before, there were no differences between simulations which used a linear or a random test of the modes to determine if the dissociation limit had been reached.



(a) **CO_2** dissociation. Park data-Ref. 8. NIST data-Ref. 9

(b) H_2O dissociation. NIST data-Ref. 9.

FIGURE 4. Prediction of dissociation rates for polyatomic gases. .

The results shown in FIGURE 4 demonstrate that the phenomenological collision-based model for dissociation can be applied to polyatomic molecules as well as simple diatomic molecules. Further study is needed to examine recombination and exchange reactions for the polyatomic molecules using the new methodologies. The computational algorithms needed to enforce detailed balance for these reactions will likely be somewhat more involved, since there are multiple modes that would need to be considered. Although somewhat more cumbersome, the direct sampling of the dissociation from each mode might be used in a manner similar to that demonstrated by Bird [1] for enforcing detailed balance for each vibrational level.

SUMMARY

The collision-based approach to modeling chemical reactions without the need to use experimental rates or to determine local macroscopic parameters such as temperature shows significant promise as a viable phenomenological approach for modeling chemical kinetics with DSMC in highly nonequilibrium conditions. The current application of the new kinetics approach to high-speed entry flows around the Orion command module predicted more dissociation of diatomic oxygen and nitrogen in the shock layer than the traditional temperature-based-rate approach and a reduction in the forebody heating at altitudes where thermal nonequilibrium effects are significant. Preliminary investigations into dissociation of polyatomic molecules indicate that similar methodologies can be applied to molecules with multiple vibrational modes, and the current study shows reasonable agreement with available experimental data for equilibrium dissociation rates.

ACKNOWLEDGMENTS

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