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A post-collision internal energy model for $O(^3P) + SO_2(X,^1A_1)$ in DSMC based on Molecular Dynamics computations

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ABSTRACT

A model is developed for determining molecular internal energies after $O(^3P) + SO_2(X,^1A_1)$ collisions in the Direct Simulation Monte Carlo (DSMC) method in order to improve modeling of the hyperthermal interactions occurring in the upper atmosphere of Io. Molecular Dynamics/Quasi-Classical Trajectory (MD/QCT) studies are conducted to generate post-collision SO_2 and post-dissociation SO internal energy distributions as a function of initial SO_2 internal energy and relative collision velocity, which are found to be an improvement over the baseline Larsen–Borgnakke (LB) method that often predicts unphysical internal energies above the dissociation energy for non-reacting collisions and under-predicts post-dissociation SO internal energy. An approach for sampling from the MD/QCT-based internal energy distributions in DSMC is developed and DSMC simulations are then conducted for a time-dependent thermal nonequilibrium heat bath using both the MD/QCT-based distributions and the LB model. When only SO_2–O collisions are considered, noticeable differences are observed for post-collisional SO_2 and SO internal temperatures.

1. Introduction

The discovery of the atmosphere of the Jovian moon Io by the Pioneer spacecraft [1] in 1973 has led to thorough scientific studies in examining its unique atmospheric physics. Its interesting atmospheric composition is primarily dominated by volcanically expelled SO_2, but also consists of O_2, SO, S, and O species formed by high energy collisional bombardment of O and its ions and sulfur dioxide. Most of these dissociation reactions occur in the upper atmosphere of Io, which is heated to thermochemical nonequilibrium via interaction with the Jovian plasma torus that flows over Io at ≈57 km/s. Since Io's atmosphere is rarefied, its planetary gas dynamics is modeled using the Direct Simulation Monte Carlo (DSMC) approach. Comprehensive planetary physics modeling through the use of DSMC by Austin and Goldstein [2], Zhang et al. [3–5], Moore et al. [6–9], Walker et al. [10,11], and Gratiy et al. [12,13] has been ongoing to study the complex phenomenology of Io's energetic, but rarefied atmosphere.

The DSMC method is a numerical approach for solving the Boltzmann equation of transport for high Knudsen number flows where the continuum fluid flow assumption fails [14]. In DSMC, the computational domain is divided into cells and filled with simulation particles that represent molecules of different chemical species. Each simulated particle represents a large number of real particles with equal properties. DSMC is based on the assumption that the continuous process of particle movement and interactions are uncoupled and every particle is moved according to its velocity at each time step. The time step in DSMC must be chosen so that the particles move only a fraction of the cell size during a time step. The interaction between particles is modeled by coarse-grained binary collision models and the molecular velocities are changed according to momentum and energy conservation of the pair. Binary collisions involving at least one molecule may be treated as elastic or inelastic, or may result in a chemical reaction.

The manner in which post-collision and post-reaction molecular internal energy is determined can have a significant effect on the thermal description of a gas predicted by DSMC. Several different internal energy exchange models have been explored for use in DSMC. The most commonly used internal energy exchange method is the Larsen–Borgnakke [15] (LB) model, which describes vibrational-translational (VT) and rotational-translational (RT) energy transfer and simulates the internal energy distribution as a continuum. For a polyatomic molecule, the vibrational modes are lumped together, giving one vibrational energy and thus not partitioning the energy into each vibrational mode [15]. Boyd [16] and Bergemann and Boyd [17] extended the phenomenological LB approach to simulate RT and VT energy exchange for diatomics, respectively, assuming discrete internal energy distributions for each.

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Gimelshein et al. [18] extended their work to polyatomic systems representing each vibrational mode as a simple harmonic oscillator.

During a collision, energy may be exchanged between the translational mode and one of the vibrational molecular modes with separate, independent relaxation probabilities for each vibrational mode. At sufficiently high temperatures, equipartition of vibrational energy between each vibrational mode is expected. The probability of a vibrational or rotational inelastic collision is $1/Z_V$ and $1/Z_R$, where Z_V and Z_R are the vibrational and rotational relaxation collision numbers, respectively. Temperature-dependence on the relaxation collision numbers was investigated by Parker [19] for Z_R and Millikan and White [20] for Z_V. However, limited data at high temperatures leads to uncertainty in these collision numbers for use in modeling highly nonequilibrium conditions. Furthermore, sampling post-collisional energies from the local equilibrium distribution function for hypervelocity collisions presents two additional issues. First, the equilibrium distribution function does not represent the physical distribution of molecular internal energies in strong thermal non-equilibrium condition. Second, at sufficiently high temperatures, the equilibrium distribution function predicts molecular internal energies much greater than their respective bond energies and are therefore unphysical.

In the Ionian DSMC simulations of Zhang et al. [3–5], Walker et al. [10,11] and Moore et al. [6–9], the continuous LB method was used to model SO_2 RT energy exchange and the discrete Bergemann and Boyd method was used to model SO_2 VT energy exchange, thus meaning that each SO_2 vibrational mode was treated independently rather than as a lump vibrational energy. The vibrational relaxation collision numbers for each mode were taken from the experimental work of Bass et al. [21] for temperatures ranging from 290–1090 K. Constant values of Z_{V,ν_2} of 300 or 158 were used for gas temperatures less than or greater than 800 K, respectively and temperature-dependent Z_{V,ν_1} and Z_{V,ν_3} values were fit to a Millikan–White form. The Jovian plasma torus heating is expected to produce hyperthermal upper atmospheric temperatures above the studied range of Bass et al., so the validity of using these relaxation numbers based on relatively low temperatures is unknown.

In summary, the models typically used in DSMC simulations of Io to determine post-collision molecular internal energy depend on the thermal equilibrium assumption and the use of relaxation numbers fit to low-temperature experimental data. However, the upper atmosphere of Io interacts with the hypervelocity Jovian plasma torus, producing thermal nonequilibrium and significant heating. Additionally, the majority of Ionian astronomical observations come from remote sensing of radiation such as the mid-infrared spectral observations from the NASA Infrared Telescope Facility of absorption in the SO_2 ν_2 vibrational band [22]. Due to the limitations of the commonly used DSMC models for determining post-reaction and post-collision internal energy, we have developed a new internal energy exchange model for SO_2–O collisions based on accurate theoretical calculations. The Molecular Dynamics/Quasi-Classical Trajectory (MD/QCT) method will be used in this work to determine continuous post-reaction and post-collision molecular internal energy distributions, which can then be used directly in DSMC, replacing the commonly used phenomenological models.

Previously, Parsons et al. [23] conducted MD/QCT studies on SO_2 + O collisions to determine collision cross sections and reaction probabilities for use in DSMC. Reaction probabilities and collision cross sections were determined for collision conditions expected in the Ionian atmosphere. The collision cross sections were subsequently fit to the variable hard sphere (VHS) [14] form commonly used in DSMC. The new collision cross section based on the MD/QCT results was found to be significantly higher than the baseline cross section by more than a factor of two. In DSMC simulations of hypervelocity atomic oxygen colliding with plumes of sulfur dioxide outgassing from a sphere, a very simplified model of the Io planet, the case using MD/QCT-based collision cross sections predicted less penetration of the plasma torus particles into the lower Ionian atmosphere [23] and a diminished gradient in the upper atmospheric temperature rise [24] compared to the case using baseline VHS parameters. It was further found that the dominant reactive process for SO_2–O collision is dissociation of SO_2 to SO and that the MD/QCT results predicted less dissociation than the total collisional energy (TCE) model based extrapolations of the low-temperature reaction rates determined experimentally by Grillo [25]. The TCE model[14] is the widely used in DSMC to simulate chemical reactions between gas-phase atoms and molecules. Complete atomization of the SO_2 molecule becomes significant above relative velocities $\approx$20 km/s, indicating that this reaction is likely to occur in the Ionian upper atmosphere and dissociation to O_2 and formation of SO_3 were found to be negligible processes. Finally, in similar DSMC simulations related to conditions of Io's atmosphere, it was found that the MD/QCT reaction probability predicted approximately half the SO_2 dissociation than the TCE probabilities [23,24]. In summary, it was found that the MD/QCT studies provided vastly different collision and SO_2 dissociation models for hypervelocity collisions expected in the Ionian upper atmosphere over the baseline models and could therefore greatly improve the fidelity of full-scale planetary simulations. However, the updated DSMC simulations with the MD/QCT models still employed the use of the traditional Larsen–Borgnakke approach for determined post-collision and post-reaction molecular internal energies.

In this paper, SO_2–O collisions are simulated for conditions expected in the Ionian upper atmosphere using the MD/QCT method to generate post-collision SO_2 internal energy and post-reaction SO internal energy distributions. Then, new DSMC procedures are developed to determine post-reaction and post-collision internal energies for SO_2–O collisions using the MD/QCT-generated distributions. By coupling the new MD/QCT-based SO_2–O internal energy exchange models in DSMC with the MD/QCT-determined total cross sections and reaction probabilities from Parsons et al. [23], a consistent approach in modeling SO_2–O collisions will be attained, in which the most significant collision dynamics are determined solely from MD/QCT results using the advanced ReaxFF potential energy surface. The effect of the new MD/QCT-based internal energy model will then be determined by comparing thermal nonequilibrium heat bath results to those obtained using the traditional phenomenological LB model, where both models use the MD/QCT-computed SO_2–O total cross sections and dissociation probabilities from Parsons et al. [23].

2. MD/QCT methodology and simulation conditions

The governing equations for the MD/QCT method are Hamilton's equations

$$\dot{p}_{i,j} = -\frac{\partial V}{\partial r_{i,j}}, \tag{1}$$

$$\dot{r}_{i,j} = -\frac{p_{i,j}}{m_i}, \tag{2}$$

where V is the system potential, p is molecular momentum, r is molecular position, and m is molecular mass. Using the ReaxFF approach, the system potential V is given by contributions from various partial energies and binary interactions: [26]

$$V = V_{bond} + V_{val} + V_{pen} + V_{tors} + V_{conj} + V_{vdWaals} + V_{Coulomb}. \tag{3}$$